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9 August Hermann Segera

SEGER'S COLLECTED WORKS

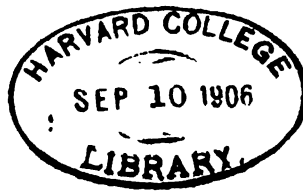
Being a Reprint of the Articles Already Published in
"Brick" and Chosen as Being Specially Helpful
to the Clayworkers of the United States

¶ Dr. Hermann August Seger was Professor
at the Royal Technical Institute, Berlin, and
Chief of the Chemical-Technical Experiment
Station, Royal Porcelain Factory, Berlin.
The original writings were prepared by Dr.
H. Hecht and E. Cramer from the records
of the Royal Porcelain Factory at Berlin.



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Introduction

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PREFACE.

The influence of Dr. Hermann August Seger upon the American clayworking industry will not be valued at its true worth for many years to come. Dr. Seger contributed his articles from time to time to the "Thonindustrie Zeitung" and the "Notizblatt," without any ulterior view of their publication in book form. They represent the result of many investigations of a mind whose aim was the reduction of clayworking methods to an exact science. The extent of his researches, the depth of his probing and the clearness of his conclusions compelled the admiration of all those who have read his writings. No other man in our industry has done more to aid the cause of progress than Dr. Hermann August Seger.

"Brick" was the first clayworking journal, published in the English language, to undertake a systematic translation of this learned author's writings. In fact, the work would have been commenced long before had we not expected that it would have been undertaken by persons in a better position to devote the time and money. The first issue of our translation appeared in February, 1899, page 95, the article translated being: "The Weathering Process of the Crystalline Rock and Its Influence upon the Structure of Clay." Since then from time to time as we saw the need, we have selected the articles of the most interest to the clayworker. We are now presenting to our readers in this volume the result of our labors since that date. We have omitted from Seger's Collected Works all the articles on pottery and the manufacture of high-grade porcelain, which are out of the range of the majority of our readers, and have embodied in the volume only such articles which we consider to be helpful.



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ERRATA.

Page 25, fifth line from top should be omitted.

Page 27, sixth line from top, read "crumbs of clay."

Page 27, the last paragraph is commencement of section II.

Page 28, last paragraph, second line, read "from that which," and fifth line, read "without the water mixed."

Page 42, first line, read "according to the calculations."

Page 42, second paragraph, seventh line, read "but is short and which on drying, etc."

Page 43, in table opposite "Sand dust, etc.," under the heading "d," read "1.84" instead of "14.84."

Page 50, in table at bottom, under first "Total" column, read "100.47" instead of "100.50."

Page 81, the last five lines should read as follows: "The first operation to which the bricks must be subjected now in the kiln is that of drying and watersmoking, since they, when introduced immediately into the annular kiln, as often happens in the case of air-dried bricks, are either reduced by watersmoking or show such a decided white incrustation from the great amount, etc."

Page 83, fourth line from the top, read "a special firing is unnecessary," and fifth line from the bottom, read "two edge-roller grinding, etc."

Page 87, on the middle of the page, the line commencing "developed heat is communicated" has been repeated.

Page 94, third paragraph, seventh line, read "cost of plant and labor, etc."

Page 104, last paragraph, ninth line, read "Saarbrucken" instead of "Laarbrucken."

Page 107, last paragraph, fifth line, read "into a mass in any degree cohesive."

Page 108, second paragraph, ninth and tenth lines, read "The dry pan, with its crushing surfaces" instead of "The crusher, with its plates."

Page 112, "Table A," under the heading "Kaolin from Tremosna" read for "Magnesia" "0.41" and for "Potassium" "1.60." In the opposite table, "Table B" under the same heading, read for "Alumina" "1.09" instead of "1.99."

SEGER'S COLLECTED WORKS.

Page 115, under the heading "Kaolin from Lettin," read for "Magnesia" ".66" instead of ".86."

On pages 116, 117 and 118, "Dr. Sarnon" should be read "Dr. Sarnow," and "Herr Bunzli" should have the u spelled with a umlaut.

Page 120, Table D, under the head "Insoluble in Sulphuric Acid," read for "Sulphuric Acid" "54.84" instead of "54.87," and under the "Total" in section IV, read "99.90" instead of "79.80."

On page 121, under section "X" in the "Total" column, opposite "Potassium" read "3.06" and opposite "Loss in Burning" read "6.55."

Page 122, Table E, section II, opposite "Feldspar Residue" read "2.49" instead of "2.47," and section IX, opposite "Quartz" read "57.15" instead of "57.17."

Page 144, fourth paragraph, fifth line, read "absorption is always indicated," and in the fifth line from the bottom of the page, read "during the heating caused."

Page 151, second paragraph, read "the dryness of the wares, the strength of the draft, etc."

Page 190, second paragraph, seventh line, read " $108.747 \div 7487 = 14.5$ kg. coal, or 108.747, etc." Fourth paragraph, last line, read "133.704 thermal units."

SEGER'S COLLECTED WORKS.

The Weathering Process of the Crystalline Rocks and Its Influence Upon the Structure of Clays.

The disintegration processes to which the masses of rock forming the earth's crust are subject, through the ceaseless energy of water and the atmospheric elements, produce new forms of matter, and this constant evolution provides us with rich material for observation and investigation, particularly to those of us who are engaged in any branch of industry the object of which is the production of articles made from clay. Although this theme has been treated more than once in a thorough and scientific manner, it does not seem a useless task to consider it again, for by regarding the subject from different points of view there is a greater likelihood of our understanding a material that is so rich in variations as is clay.

Nowhere does nature, whether organic or inorganic, stand still. Matter is eternal, but its form, as we meet with it, is subject to continual change. That which stands before us, scarcely even completely built up, begins to disintegrate through the unresting forces of nature; its constituents in everlasting changes become rearranged as new material. Even the most durable stone, to which from our superficial observation, we are inclined to attribute unending duration, because in the short time that man can observe no change can be seen in it, is not able to withstand the action of water combined with oxygen, carbonic acid and with changes of temperature, and it has to submit to a change either of form or of substance, or it may be that it is completely disintegrated and redistributed. We understand by the word "weathering" that process of disintegration of a stone where chemical and physical influences remove a portion of it, loosening its particles and reducing their cohesion so that it is possible for natural mechanical forces to carry away the product to distant places and redeposit it in the shape of stratified rocks. The multifarious character of the chemi-

co-physical properties which produce the changes, and the local conditions which frequently modify the processes of disintegration, allow a great number of forms to result and offer endless difficulties for the observation of them from any one point of view, that so far the sciences that have assisted in the investigation of the subject have not yet been able to bring order out of the chaos of properties, of rules and of exceptions that will enable the clay industries to employ with full confidence the scientific conclusions and to get that counsel from them which is in such a high degree necessary for its full development.

The high resistance mostly found particularly in the crystalline rocks, and the low energy of the disintegrating forces, causes the process to cover an enormous extent of time. This makes it difficult to study the phases that any one material goes through, so that a proper presentation of the matter can only be obtained by means of an extraordinarily large number of observations, and it is to this very slow development in no less degree than to the difference in the original material, and the way in which the disintegration was performed, that the immense variety in the character of our clays is to be ascribed. If in any one particular mineral we consider the stages of disintegration in regard to chemical character and physical condition, then this study, while it gives a general insight into the chemical properties, as also into the structural condition of the product of disintegration, yet gives us a very undecided view. This is because the process of disintegration is not all carried through in one place, but in different places and at different times, so that it is almost impossible to find the direct cause for an existing appearance.

In consequence of their chemical nature, not all the constituents of the crystalline rocks are able to produce clay as the result of weathering. Probably in no case do the clay-forming rocks have the time or the opportunity to go through all the stages of disintegration up to the final one, and give us that which has hitherto been a hypothetical material—the pure clay-substance—but stops short at some intermediate stage which only approximates more or less closely to the last stage. Accordingly, we find along with the clay, taken in the broadest sense, broken-down rock, gravel, sand, silt, loam and loess. Or, on the other hand, where the process of weathering and crushing has been interrupted, we find the original rock, an upsetting and mixing together of portions with the smaller particles cemented together again—without, however, the introduction of any new material—in the form of conglomerates and breccia, sandstone and shale; perhaps also crystalline stones again

in every possible stage of chemico-mineralogical and physical variation. Of all the primeval rocks which give us material for the formation of clays, exhaustive investigations have only been made of the group of feldspathic minerals, or rather of the rock masses formed from them and the weathering processes to which they have succumbed, while the chief materials or minerals which produce common clays, or which give to common clays their peculiar characters and distinguish them from pure clay, still rest in deepest darkness, and an exhaustive enlightenment of these conditions remains as the subject for further and very extensive investigation. The investigations into kaolins and plastic clays that result from the disintegration of feldspar and kindred minerals, for which we are indebted to Brongniart, Forchhammer and Bischof, by no means justify us in forming conclusions as to the properties of those claylike materials that are derived from augitic, zoölitic and volcanic metamorphic minerals, and even though valuable hints may be given for the further investigation of these substances, it cannot be denied that at present we are very far from having acquired that enlightenment that practice needs and science insists upon. Although we are not able to exactly determine the chemical relationships existing between the clays and the rocks from which they come, we have one fact, that is, parallel structure, which is common to all the disintegration products of the crystalline rocks. This is of the greatest interest to the industries concerned in the exploiting of clays, whether we find this is complete stratification and shale formation, as is the case with many alluvial clays, or whether it is only noticeable for short distances, as in kaolins.

A property of matter which greatly influences the internal structure of a deposit of clay is this, that all crystalline bodies show unequal cohesions in different directions, and this differentiation in the internal structure of the crystal determines its facility for cleaving in any particular direction in proportion as the axes of the crystal diverge from each other. It is only in the crystals of the regular orders that we find complete equilibrium in the mutual attraction of the smallest particles, which exhibit cohesion in three different directions, while in all other crystalline formations, that is to say in the great majority, the cohesion of the mass is in one or two certain directions peculiarly weak. What I wish to call attention to is the influence which this cohesion difference has upon the structure of the clay deposit. I am not taking into account the other properties of clays, as this particular property, with the exception of plasticity, is the only one that is common to all clays, and it is capable in so eminent a degree of increasing the technical difficulties of working

the clay. We must agree that it is the feldspathic rocks that provide, by their disintegration, the material for kaolins and plastic clays, as well as an important portion—the most refractory—of the common and brick clays. They exhibit the quality of unequal cleavage in a very remarkable manner, and when considerable proportions of soda or lime are present, are greatly subject to the destructive influence of the atmospheric elements, so that the conditions in question can be best observed in this connection.

The process of disintegration of the feldspathic constituents of the crystalline rocks begins—as a rule, with some few exceptions, where the contrary has been observed—on the surfaces of the separate and individual crystals, and shows itself in a matt or corroded appearance of the surface and a cloudiness or dullness of the mass. If the crystal in this first stage of disintegration is examined under the microscope, we shall see that to a greater or less depth it exhibits countless extremely fine cracks. These are particularly noticeable in the direction parallel with the planes of easiest cleavage. Through the influence of water and the carbonic acid in solution in it, some of the constituents—alkalies, lime, silicic acid—are carried away, and the mineral, taking the character of a pure potassic feldspar, becomes completely converted into clay and loses about 53 per cent of its weight. It is clear that with such a loss of substance, even in the earlier stages of disintegration, either a shrinkage must take place in the mass or there must be a separation of the particles. The first is contrary to both theory and observation. In a rearrangement of the particles, which is accompanied by a loss of cohesion, the breakages naturally occur in the direction in which they have the least mechanical resistance to overcome, that is to say, in the direction of the principal cleavage planes. It is a generally observed condition of all the operations of chemical affinity that the degree of this operation is considerably influenced by the physical condition of the material, and that an important factor in the difference in molecular attraction is caused by the condition of cohesion. A substance which, in a very finely divided state or loosely combined, is energetically attacked by reagents, will always exhibit a lower and sometimes a greatly reduced combining energy if it has passed over into a denser or a crystalline condition. Crystals, too, do not offer an equal resistance in all their parts to chemical action, but are easiest attacked from those sides where they possess the least density and cohesion. The easier cleavage of the feldspathic rocks indicates the direction in which the chemical attack would take place; the breaking up of the crystal into a number of thin plates, the entrance and the destructive effect of water, would be

particularly favored, so that it is clear that, until the mineral has passed into the condition of clay, it will divide up into thinner and thinner flakes, which at last attain the extreme limit of fineness, as the glistening particles of silt so often show.

The influence which this more rapid progress of disintegration, in a certain direction, has upon the structural conditions of the product is less noticeable when the mass remains in one place than when there is a change of position. The products of disintegration, when found upon their original beds, show the original structure of the rock from which they result, although their features may be drawn and deformed by loss of substance and volume. In the great majority of cases, except where the whole of the feldspathic material has been transformed into formless clay, we find a cleavage corresponding to the original crystalline structure, and brought about through the feldspathic detritus lying in parallel planes; but this parallelism does not go beyond the limits of the original individual crystals, and we may not find it at all if there has originally been a very fine-grained crystalline texture; but if the separate and original individual crystals had not been in parallel layers, the resulting clay deposit will never exhibit a stratified or shale-like character. But if, in addition to the disintegration or weathering process, a slumping process had taken place, the structural conditions of the clay will not be the same. The horizontal parallel structure of alluvial clays is brought about by the presence of layers, which both in chemical and physical conditions differ from one another, though lying close together, so that at different heights we find deposits with sand, silt or clay particles dominating, which in themselves again show variations of grain, permeability to water and plasticity. Also through the mineral detritus which has attached itself to the layers, differences may also be produced by the presence of residuums of crystals in extremely thin scales, in which the extraction of the alkalies and the loss of crystalline structure has not been completed by the weathering process.

A small piece of rock, ground off mechanically and carried away by water, we are in the habit of calling, when it attains a certain degree of fineness, a grain of sand; this we do, no matter what its mineralogical character may be. This grain of sand, as a rule, has a spheroidal or polyhedral shape, and when laid on a horizontal surface in a position of stable equilibrium, may lie in a great variety of directions; but it is different where the thinnest possible flakes, produced by chemical action from pulverized particles of crystals, are gently carried by water in company with formless clay particles, and so escape the breaking up caused by rolling and grinding.

Where these lamellae settle at the same time as the clay, we cannot conceive of their taking up any other than one position on the sedimentary surface, that is a horizontal position, because these particles have practically nothing but an upper and a lower surface, and in any other position would find no support. The consequence of this is the special parallel structure of the individual crystals, though not the structure of the crystalline rocks as a whole, is reproduced in the total sediment, whether this be clay, or by a later metamorphosis shale clay, clay shale or micaceous shale, and the integrity of the sediment will only be spoiled by the irregular and accidental presence of mechanically splintered rock detritus and of amorphous clay particles. The presence of immeasurably thin and dust-like mineral particles, with forms approximating in a certain structure to that of the clay mass, may be followed in all its variations with the help of the microscope; but for our industry the disturbing effect of the weakening of cohesion and the reduction of plasticity is very much less felt where the kaolin and unstratified plastic clay are found on the place of their original formation than in the alluvial deposits of clays, loams and marls.

It seems remarkable, in face of the evident importance of physical condition, that in the majority of the investigations of clay materials so little account is taken of this, and that no regard is paid to the chemical difference between particles that may frequently be seen even with the naked eye; on the contrary, all is lumped together, or if an endeavor is really made to separate sand, silt and clay, nothing more than this is done, with some few exceptions, than to note the relative weights, without entering into the question of the properties of the substances. If we have in the earlier years of the existence of the "Notizblatt" had our attention continually called, by the writings of Turrschmidt, to the need for studying the properties of clay from every point, and particularly from the physical side, it seems to me that, considering the deficiency of our knowledge, this urgent insistence is by no means superfluous. Science finds itself in this domain, in face of the demands of practice, in a somewhat helpless condition, not so much because the aim for which it strove was indefinite, but because so far the methods failed to give those results that, for the ceramic industries, were of real practical value. Clay-like matter that is used for glass and cement manufacture has its characteristics destroyed to such an extent as to become quite unrecognizable, so that the determination of their physical properties is of much less importance than of that for the production of ceramic ware; indeed, we may say that the "en bloc" analysis of clays, as it has hitherto been done, has for the practical clayworker

next to no value whatever, unless in addition to the chemical analysis a worthy place is given to the mechanical analysis by the use of the slumping apparatus and the microscope. Only then, when these voids in the older and imperfect investigations are filled up, or a new series of sufficient extent has been produced, in which more account is taken of the physical side, can conclusions be formed as to the important characteristics of clays, and the conclusions drawn from the scientific results will be of assistance to and command the respect of practice.

The Formation of Crystals and Its Significance for the Clay Industries.

The demands made by the manufacture of cement, and by the ceramic industries in respect of the composition of clays, are as different as are the objects which these industries pursue. In the manufacture of portland cement we have in the first place to keep in mind the attainment of a product of a definite chemical composition, and since the characteristics of the clay as such must entirely disappear, we have above all things to regard the relative behavior of the individual elementary constituents, and the physical condition in which these exist have only to be considered from the point of view of the greater or less difficulty presented to the complete breaking up of the clay character. The clay industries, on the contrary, have an entirely different object in the treatment of their raw materials. The limits within which the chemical constitution of a clay may vary are very wide, and as the clay-like character of the material has to be retained, its physical properties and those of its allied and accessory constituents are what we must place more in the foreground. While for such purpose the chemical composition of a clay appears rather a matter of indifference and of chance, in so far as it depends upon the mutual relationship of the clay, silt and sand, and also of its adventitious constituents and their elementary chemical composition, the physical properties of these, the grain, the form, capillarity, plasticity, melting point, etc., are of greater importance, and the chemical character of each constituent is only to be considered in so far as it enables us to arrive at a conclusion as to the physical quality of the whole. It is certainly a serious mistake to treat materials that chemically and mechanically are so non-homogeneous as the clays and earths employed in the ceramic industries in the same way as a chemically and physically homogeneous material, such as glass, for instance, and draw our conclusions as to its properties from its elementary chemical composition.

The chemical changes which occur in the material used in the ceramic industries are of minor importance, except the loss of the chemically combined water, which destroys the plasticity of the clay. The material does not lose its earthen character in the measure that glass or cement does. Above all things, it appears desirable that investigations of the chemical composition of the clay, as a whole, should be discontinued, and in place of this a deeper study should be made of the composition of the separate constituents, the principal and the accessory, in order that a conclusion may be drawn as to the whole from a consideration of the components. Taking one instance, we have no need to inquire how much alumina and how much silica we have in our clay, but what proportion of the alumina and silica falls to the sandy portion and what to the silty or clay portion, and after we have found this we determine the physical properties separately of the sand, silt, clay, etc. The accessory or adventitious constituents of a clay possess a no less important influence upon it than its main constituents, as their chemical action, which generally is slight, yet can produce changes in the clay mass that cause very unpleasant results in manufacturing.

It has been said above that on considering clay materials from the ceramic standpoint, the physical conditions of the whole should be put in the foreground; and on the other hand the chemical character does not justify us in forming any conclusions, but only becomes of value when the non-homogeneous mass is separated into its distinct portions, the chemical properties of each, with the physical characters based thereon, should be found. In this matter a way is indicated which demands a very much more complicated process of investigation than has hitherto obtained, but which justifies us in forming much more far-reaching conclusions than the "en bloc" clay analyses that have been customary for technical purposes. If we have in individual cases made a separate investigation of the clay substance alone, considering all the other constituents as under one head and leaving them unnoticed, this was quite right where the object was a purely scientific one, with a special object in view; but in treating the materials that are intended for technical purposes, the adventitious materials, which are often present in greater quantity than the clay substance; have as much reason to have their properties determined as the clay itself has.

It cannot be denied that the investigations of clay have supplied us with scrupulously exact analyses of materials, but that very little has been learned as to the structure, plasticity, capacity for absorbing water, shrinkage in drying and burning, shape and size of the sand and silt grains, peculiarities in balling and laminating, and the

throwing out of salts and efflorescence generally. If, as I proposed at starting, that for the purposes of the clay industries the properties of clays should be regarded from the physical rather than the chemical standpoint, then it will be allowed me in this place to throw some light upon the working of a force which has the greatest influence upon the properties of clays and the articles made from them—a force which, like no other, works secretly and in concealed ways, slowly but surely, and which can produce the greatest changes and disturbances; that is the force with which the smallest particles of similar matter strive to lie close to each other in geometrically bounded forms—the force of crystallization. We will have to consider this influence from several points of view, as follows:

1. With reference to the structure of the raw materials.
2. Upon the further capacity of the clay for weathering and melting.
3. Upon the capacity of crystallization for destroying the finished ceramic product.

I.

If we find as the result of a great number of investigations and of innumerable observations of the weathering of crystalline rocks, which gives us the varied group of products that we know as clays, shale clays and clay shales, and attribute their origin to chemical reactions, mechanical splitting up and breaking down by rubbing and grinding, the thought occurs to us that the reversal of this process may take place, such as chemical science frequently offers examples of—the regeneration, by rearranging the separate particles in new combinations, and by taking up again by new infiltrations the substances lost in weathering. These speculations bring us to the structure of some of the porphyries, which have the undeniable character of rocky strata resulting from sedimentation, as they strikingly exhibit in the shale formations of gneiss and micaceous shale no less than in the transformation stages to be seen in many places of the clay, through clay shale and micaceous shale up to the feldspar rock. If we keep all these rock products together, without regard to their chemical constitution, and only bearing in mind their physical conditions, we get an unbroken series of similar peculiarities, appearing in varying potencies, which lead us to this position, that the results are produced in one way common to all, and the differences in the products can only be ascribed to the degree and the time of the action of those forces which have impressed upon them the changes they have undergone, without entirely obliterating their characteristics. In the same way that we can follow in an unbroken series of stages the weathering process, from the solid crys-

talline rock, whose cohesion is destroyed by weathering, along through gravel, sand and clay, in the same manner we can follow, by the reverse way, the building up from the debris of the rocks, of solid masses of shale, sandstone, conglomerates and breccia until we get to the formation of unmistakable crystalline structure.

Although nature has not freely permitted the human eye to get an insight into her most secret workings—although she does not show us how clay is turned into clay shale, sand into sandstone and wacke, or how from the deposits of limy shells of animalcules a crystalline lime, or marble, is formed—though she has not up to the present time permitted us to discover the conditions under which a heap of mineral debris becomes anew a crystalline formation, yet the speculations of science enable us to get an idea of the way in which the change may have come about. We make a comparison between the products upon which the same unknown influences, of unequal duration and intensity, have operated, and by this means we can get somewhat nearer to the unattainable workshops of nature.

It has not been possible for us to watch the growth and being of crystalline substances, which, as we see them in our daily life, seem impossible of solution as liquids, yet these may be seen as accomplished facts in every block of rock. These, too, show with their accompaniments the way they lie and their structure, that they must have been formed under different conditions from those which were present when science was fortunate enough, by artificial means, to make some imitations of them; for this reason, that the processes of nature are carried on very much more slowly than are the operations of science, which is compelled to use more active agents, for human observation of the processes of nature is restricted to a very short period of time.

As has been said, natural science does not yet stand upon such firm ground as to be able to explain to us definitely and clearly the required conditions under which formations on the earth's crust would take other forms. It seems the explanations, so far, have rested partly upon a blind belief in authority; these have hindered true investigations, or they are built up of theory based upon insufficient observation, which today or tomorrow may break down under the pressure of new facts.

I do not consider that this is the place to discuss the differences of scientific men as to the origin and changes of the rocks, or to weigh the pro and contra of the opposing views that are held but will confine myself to practical matters, inasmuch as I will only

speak here of transformations that take place in the clay material and the influence which these may have upon its physical properties, and if I am compelled from time to time to take into consideration other descriptions of rocks, it will be for the reason that some of the peculiarities common to clays are exhibited in these in a more striking manner.

If in what has been written the influence has been shown of the crystalline condition of a rock upon the structure of a clay which has been produced by disintegration and washing away, we have only got so far as the regular horizontal strata; these in nature form the exception; the other structural conditions, the concretions, ballings, compressions, find therein no explanation. It is a singular force and one that, in different combinations, exhibits a multitude of variations in its intensity—a force which, when the aggregate condition of the molecule attains a certain form of motion, that is, when from the fluid or gaseous it passes to the solid form, compels similar materials to take up such positions relatively to one another that bodies result that are bounded by regular surfaces, which are always at similar angles to each other, and that this effort to deposit in a similar manner—therefore to form in the largest possible individual crystals—in many cases is so great that the act of crystallization may be accompanied by exhibitions of enormous force. The attraction of the smallest particle of crystallizable matter, which gives rise to crystallization, always finds in the inertia of surrounding medium an opposing resistance, and if the action of molecular attraction upon the medium is not always alike, the reason for that is that it is possible for both the attraction and the inertia, according to the properties of the material and the predominating conditions, to vary within the widest limits.

It is, perhaps, not superfluous to mention that crystalline form consists less in the development of a mathematical outline, but much more in the presence, in the mass, of a structure corresponding to a certain extent to the arrangement of the outward surfaces. This shows itself, in most cases, in a cleavage in one or more directions, which, in crystals of similar material and formation, is always constant. A body that is bounded by level surfaces is not by any means necessarily a crystal, but only becomes one when the outer bounds are an expression of the internal structure. On the other hand, the great mass of crystals found in nature do not show these strikingly bright surfaces, with the exception of comparatively rare specimens preserved in museums; but notwithstanding this, these minerals may be crystals if the arrangement of the mass is crystalline, and, as a consequence, the internal arrangement has this

special character, while the outer surfaces may, for want of room, have been unable to develop. It need not, therefore, appear strange if we find crystalline material possessing all the properties of crystals except that of mathematically defined crystalline surfaces.

As has been said above, the formation of any crystalline substance presupposes a certain mobility of the molecules in order to set according to a definite system, and where this is wanting—that is, where every portion finds itself in a rigid condition—then an outer mechanical effect is required, as, for instance, in the crystallization which has been observed in railroad axles as the result of long, continued shocks and jarring. In general though we may say that, for the formation of crystals, it is necessary for one of the mediums to be a resolvent in order to insure the necessary condition of mobility of the molecules, and in fact the crystals occurring in nature give evidence of the co-operation of a resolvent fluid, except the actual volcanic products, in which other conditions play a part. The resolvent fluid that occurs in nature can be nothing else but water, and its power of dissolving is enhanced by its containing carbonic acid, oxygen, organic substances and salts and by an increase of temperature. We will therefore in this place have to observe principally the influence of water as a medium for the evolution of clays and note its effects upon their structural conditions.

It has been long known that salts in solution, even when present in small quantities, will bind together into a solid mass any finely pulverized but insoluble material which is in the same solution, while, in the absence of such powdered matter, the salt solution will dry into a loose and friable mass. We regard a clay shale and its allied rocks in general as a deposit of clay which has hardened, and this hardening has, in most cases, been brought about by the settling of feldspathic matter, which has partly altered the original clay substance and partly cemented it together. How this cementitious matter has got into the clay deposit, or has formed itself out of this, is a disputed point which has been energetically discussed by geologists, but in which the weight of reasoning appears to be in favor of those who contend for the action of water, with, perhaps, an elevated temperature, while the champions of the metamorphosis by the simple action of fire begin to find themselves in a very difficult position.

In observing the structure of clay deposits, we not only notice a division in a horizontal direction, which is recognized at the first glance as a consequence of sedimentation, but we also find other appearances which teach us that after the deposition still further changes took place in the material. These changes may be set down

as those of purely chemical action—those that are brought about by the action of water and those that are mechanical. In the latter case they have mostly their foundation in a chemical process. After the conclusion of the disintegration and slumming processes, which the clay from the primal rock is subjected to, the chemical action of the water and the atmospheric elements do not cease; but this action is carried still further, depending upon the conditions, so that a further disintegration or leaching takes place, or else certain materials are dissolved and carried to another place, or deposited upon similar matter, so that we may have a transposition of certain constituents within the clay itself, or there may be an introduction of foreign matter and a fixing of this in the clay substance. In all these cases water as a vehicle plays a very important part, but its successful working depends upon a condition which is of the greatest consequence—that is, the necessity for its circulation being in the direction assigned to it by the formation of the clay deposit. Clay in the moist condition behaves like no other formation from rocks, inasmuch as its strata are watertight and withstand the passage of water, so that the circulation of the latter is only possible between the layers of clay and in the runs or cracks caused by the interdeposition of foreign matter, particularly vegetable matter, and through the cracks that have been produced by pressure.

This limitation of the action of water appears to be of the greatest importance to the changes taking place in the city, for the removals, new formations and concretions which take place have a definite direction given to them by this restricted circulation of the water. We know that the filled-up cracks and hollow places which we are able to note in hard rocks have a material deposited in them which, according to its nature, shows a structure that is either in bands that will flake off more easily in a parallel than in any other direction, or else it exhibits a cleavage at a certain angle to the direction of its length. The latter case occurs mostly when the substance that fills the channel is found in a crystalline condition. The reason for this is that there being only one direction for the crystallizable fluid, the individual crystals all took up one certain position.

If we carry over this teaching to the process of hardening of a clay to a clay shale, whether it be through the introduction of new matter, through the water forcing itself in, or whether it be that the cementitious matter is taken from the clay itself, then as the circulation of the water takes place through infinitely fine and horizontal cracks lying very closely together, the horizontal direction of the cementation will become more pronounced and exhibit a true shale construction, while by a rearrangement of the mass of the binding

material at a certain angle, the original stratification becomes weakened or may disappear altogether, and in its place we get a secondary or so-called false shale.

Daubree sought for an explanation of the behavior, the compressions and the secondary shale formations in sedimentation, and believed that it had to be ascribed to the effect of mechanical pressure produced by its own weight—as the layers are often very thick—and the pressure of the mountain masses resting upon it. This opinion has certainly some justification, for we always see that under mechanical pressure, if the cohesion of the compressed body permits of the smallest change of form, a stratified structure is brought about which always runs parallel with the plane of compression. As an instance, we may see this structure in iron when it is rolled or drawn, for upon etching it with acid, this characteristic arrangement of the material always appears. In rolled plates it is a platelike formation, in drawn wire it has a longitudinally fibrous appearance, which is at once seen to be the effect of pressure.

But this explanation will not suffice for all cases, and it will not explain how this pressure of the material is carried forward so equally through an immovable mountain mass, so that the direction and strength of the dips and false shale formations remain constant, while in other instances of this kind we remark the effect of pressure. It is very quickly reduced in the interior of the mass, and especially near the upper surface. We can see this reduction in rapid progression even in soft clay, which on the potter's wheel is subjected to a pressure on one side. If we examine with a magnifying glass the fracture of a shard of a piece of thrown ware, we will find that, as a result of the working, a parallel structure has been produced, that the grains of sand and silt under the pressure of the hand have taken up such positions that their longest dimensions are in the direction of motion and pressure, so that they are arranged parallel to the outer and inner surfaces of the shard, but at a very few millimeters distance from the surface this structure loses its strength, and in the middle of a tolerably thick shard it is no longer to be seen. But in what takes place in nature we have another operation to note—where a pressure is exerted upon the hardening mass of clay, and this lies in the hardening process itself, in the pressure which the cementing substance exerts upon the medium containing it during the process of crystallization.

Enough examples are known of the force with which crystallizable matter attracts similar matter upon its surface in the effort to enlarge its crystals, and if space is wanted for this it will make it by thrusting, or else will take up foreign substances mechanically be-

tween its lamellas. The pressure produced by the formation of crystals is so great and so continuous that it is impossible to imagine anything more powerful, so that this force has been suggested, very likely with perfect justice and with the greatest probability, as the sole or at least as the chief cause of the lifting up of our mountain ranges. It is very clear that such a force, when it acts in the interior of a mass of clay, must have a profound influence upon its structural formation, and we may add to this the pressure of a crystallizing cement, which has been introduced in the act of sedimentation by the water carrying the crystal-forming matter in solution; this water moving only in one direction, it need not appear strange to us if the effects in similar strata remain remarkably constant. As the structure-forming pressure is exerted by the planes of the crystals—the infinitely small crystalline particles which bring about the cementation—the cleavage, nevertheless, does not stand in quite a simple relationship to the outer surfaces, so that, as a rule, we cannot form a conclusion from the structure as to the nature of the cementing material, but can only note towards which side the greatest pressure was exerted by the act of crystallizing.

In clay deposits and the allied rocks we often meet with concretions which, from their color, structure, hardness and plasticity are strikingly different from the accompanying material and are, particularly for the clay, of the greatest importance, because they put serious difficulties in the way of attaining that homogeneity which is so necessary for every kind of ware made from clay. The most varying explanations have been offered as to the origin and nature of these appearances, but none have been quite satisfactory. One thing is certain, that they cannot all be brought under one head, for their structures differ very much in kind. Some are in concentric scales, some in horizontal planes, others projecting at regular angles to other cleavage planes, others again, without any regular stratification, are interwoven with veins of lime or iron oxide. It has been supposed that these formations are to be regarded as partly secondary disintegration products of feldspathic minerals, partly as products of the drying and shrinking within the clay itself, and partly as new formations or the commencement of the existence of feldspathic crystals. Their aspect teaches us that these concretions are not always secondary disintegration products from feldspathic rocks. They possess the property of clay, of holding a certain quantity of water by surface attraction and of offering a certain resistance to taking up any more water; they are, therefore, water resisting, often to a much higher degree than the clay that surrounds them; besides this, they often show themselves

to be more plastic than the clay, and require a very troublesome manipulation to mix them well with the clay and get a fairly homogeneous material. These concretions would not show such characteristics if they were secondary disintegration products or were still in the disintegration stage, for we know that feldspar, on passing to the state of clay, loses 55 per cent of its weight, or 33 per cent of its volume; besides this, the product is the more plastic the further the disintegration has proceeded. According to this there must have been a hollow space giving room for other deposits, or the mass must have been in a condition of lower density than we observe it, for there is no reason for supposing that under these circumstances there could have been an increase of density.

The theory that it is due to drying within the clay deposit is still less acceptable, and we cannot attribute to this cause the increase of density and greater resistance. According to the nature of clay, drying can only take place on the surface, and this, in consequence of the shrinkage, cracks often into very regularly shaped pieces, which sometimes strongly resemble broken pieces of crystals, though they are not otherwise to be compared with crystals. It is impossible to understand how certain portions of a clay bed could give off the water by evaporation, while the clay all around remains wet. The concretions found in clays are always of greater density, and such increase of density can only be explained by mechanical pressure either from the outside or through the intrusion of foreign substances, and the increase of the substance exercising a pressure from the inside and within a certain radius, whereby at the same time a simple cementation can take place. In what way these changes take place within the clay we do not know, and there is an entire lack of positive and comparative observations upon the matter. The multiplicity in the forms of the materials, and the circumstances which bring about the alterations, are so difficult to determine that I must confine myself to simply giving a few examples.

If organic remains, such as roots, leaves and the lower orders of plants, bodies of animals, etc., are imbedded in the clay, this will give an exceptionally favorable field for the transposition of some portions of the clay, not only because these substances favor the circulation of water, but they supply the material for the formation of carbonic acid, which greatly assists the action of the water. Now, if the clay contains iron compounds, as with very rare exceptions it does, these will work in such manner upon the carbonaceous matter that in time the carbonaceous matter will be broken up and the carbonic acid resulting from it will be dissolved in the form

of a double carbonate of protoxide of iron, and in this shape, following the direction of the water circulation, it will easily be carried away. This carbonate of protoxide of iron reacts very readily, particularly when it comes in contact with a body which has a greater affinity for its carbonic acid—as, for instance, lime—and becomes again what it was before, chiefly an iron oxy-hydrate. So soon as it gets out of the active region of the organic substances it changes, and for the lost portion of carbonic acid takes a corresponding quantity of lime, and instead of continuing its journey takes the opportunity of depositing itself in an insoluble form. Where these deposits of iron oxide or lime occur, they change the clay and cement it together, and appear in the form of clay ironstone, septarian or marl nodules, or as iron and marly veins. The peculiarities in form, hardness and chemical constitution which the clays undergo in such cases depend generally upon their chemical and physical compositions, and in consequence offer a multitude of variations. The concretions which have been formed by the transference of the iron consist mostly of carbonate of lime, and as this always separates in an uncrystallized state, it very seldom effects much change in the structure of the clay, and only cements the clay substance in such manner as the circulation of the active solution permits, forming tubelike or spheroidal masses, with cylindrical or spherical shaly structure, or forms fillings, hardenings or dendritic casts in veins, cracks or on sliding surfaces.

Quite different to the simple cementitious deposit is the action of the crystalline deposits upon the clay, inasmuch as, in addition to cementing, they exercise pressure and increase the density of the clay, without necessarily altering to any extent its chemical composition. As the commonest example of this kind we may instance gypsum. Gypsum may be introduced to the clay by water, or it may be formed by the mutual action of carbonate of lime, iron sulphide and oxygen in the deposit itself, and strives, as very few other accessories of clay do, to concentrate into large individual crystals, which property is greatly favored by its comparatively free solubility in water. Gypsum is a very frequent constituent of clay, and appears in it mostly as clear, colorless crystals, often of considerable size; these are imbedded separately in the clay, or in star-shaped or spherical groups running into one another, frequently resting on marl nodules, which have given up to them a portion of the material for their formation. Where the conditions within the clay deposit are favorable to the formation of gypsum, larger or smaller crystals are produced, and where there is not sufficient space for them they make room for themselves by thrusting and compress-

ing the clay. But the action of crystalline formation does not always take place in this simple manner; on the contrary, the structural appearances indicate that the cementing and controlling crystalline deposits do not show as connected individuals, but, as we have seen in the hardening of the clay shale, in the shape of infinitely fine lamellae, lying distributed in the mass of clay and giving to this a certain cleavage at a constant angle.

It has been maintained that in some cases of increase of density in the mass of clay we could see the commencement of a feldspathic formation, and this view has been supported by the fact that the angle of cleavage of the clay, in the case observed, was very near to that of the feldspar crystal; but on measuring the angle of the so-called clay crystal it was found to show a greater divergence from that of feldspar than any variation in feldspars of different origins and constitution; more than this, an agreement in the angles would not justify us in assuming that a feldspathic formation had commenced, as the angle of cleavage might be due to the pressure of the surrounding material. In isolated instances, if the principal cleavage plane of a cementitious body agrees with its outer planes, there may be such a division that the cementitious material can be readily recognized, as, for instance, the crystalline sand of Fontainebleau, which is impregnated with calcspar, and only in consequence of this does it show the rhombohedral cleavage peculiar to calcspar.

In the same category, I think, in agreement with Beck, ought to be placed a marl observed by Camillus in America. This is a separation of common salt pyramids. A deposit of marl several feet thick is found, consisting entirely of crystalline concretions of marl, in which are hollow pyramids of common salt in groups of crystals of from one to eight inches in diameter, whose own formation in a salt solution, without breaking down before reaching such enormous sizes, seems inconceivable. I will mention another instance which appears interesting, because the formation was observed and took place within the short space of a decade. It is true that in this case the characteristics impressed upon the clay were given by a salt that has scarcely an equal in its efforts for crystalline formation. At an alum works in the Rhineland some crystallization tanks were made of plates of sandstone and sunk in the ground; beneath them and around the sides a very fat clay was well tamped, in order to prevent leakage of the solution. After several years' use the disruptive force of the solution, which had penetrated the stone, had disintegrated it so badly that the tanks had to be removed. The clay around them, which was formerly watertight, had undergone

a remarkable change; to a depth of from six inches to a foot it had entirely lost its character, and had become converted into a loose heap of octahedral pieces, measuring from a quarter to three-quarters of an inch, which held among them a small quantity of a clayey substance. These debris were easily crushed and consisted of crumbs of clab, filled with a great number of alum lamellae, in many cases containing a complete skeleton of alum, which gave to the mass of clay its outer form, while this had no relationship to the crystalline form that had been developed. The mechanical action produced by this crystallization was no less remarkable. The side walls and partitions of the solution tanks were lifted up and broken in many places, and a portion of the building, in the cellars of which the tanks were placed, had its foundation so lifted up by the infiltration of the alum solution that there was a two-and-a-half-inch crack in the building, through the door and window openings, to the crest of the roof.

Besides this, isolated formations of crystalline silicates can take place in debris formations, without our being able, so far, to state the required conditions, as is shown by the frequent appearances in sedimentary strata of mica in kaolin and sandstone, of feldspar in clay shale, of sanidine in trachyte, conglomerate of Langenberg and Lutterbach in Siebengebirge, as described by Jenzsch. Sanidine crystals—a variety of feldspar—have at most a length of one and a half millimeters; these are found in the clays derived from melapyre of Tannhof and Buckeberg, near Zwickau. Their surfaces are usually rather rough and are covered with a second coating of the surrounding clay. They are as clear as water and possess a lively glassy luster, which is very easily seen on the cleavage surface. As the melapyre sanidine there has not been received as an admixture, it must have arisen in the clay during the disintegration process or after its completion, as also the black mica scales which accompany it.

It is a peculiar arrangement in the laws of nature that the effects which are produced in accordance with them can be traced back to a very few forces and that the same force can cause an effect to cease, which itself has produced, therefore, it can work in a contrary direction. We see this very clearly in the processes and manipulations which clay and its allied formations have to undergo in order to imitate nature's product, stone, which is the end and object of all ceramic industries. According to the fundamental laws of mechanics the working of one force can only be stopped by the action of an equal and opposing force. The preparation of clay requires a body possessing greater mobility of its smallest particles, the one

upon the other, than the natural product offers us, not only that we may the more readily give to the more plastic mass a desired form, but also to destroy the inequalities in the material, due to the manner of its formation, to the separation of materials during nature's slumming process in consequence of the inequality of specific weights and, after deposition, by the molecular attraction of similar materials.

The attraction of clay to clay and water to clay, in the ordinary (clay bank) moist condition, gives our material a certain degree of firmness, a certain resistance to taking up a further quantity of water, and this is increased on bringing the molecules closer together by means of mechanical pressure, whether this is applied from the outside, or from within through the movement of some of the constituents, then this force must be broken and the methods that must be adopted depend, in the first place, upon the nature of the raw materials and in the second upon the degree of preparation which must be given to them.

If the composition of the clay and the object we propose to attain are such that solid particles contained in it cannot be dissolved by water, then we must have recourse to some method of getting rid of the harmful constituents and in such case the method indicated is slumming; if, however, from the nature of the material, it is believed that this process can be dispensed with, then, at least, a loosening of the material is necessary, in order to give the water, that has to soften the materials, access to every part and let it do its share in producing the greatest possible homogeneousness. The equal incorporation of the water by simply soaking and afterwards mechanically working it, has been proved in practice, in most cases to be insufficient unless this is done in the most painstaking manner and one of two methods must be adopted to overcome the resistance which clay exhibits to the taking up of more water and these are, either drying the clay, or freezing it.

Air-dried clay behaves very differently under the action of water to that which has a certain quantity combined with it by surface attraction; while the latter offers the greatest resistance to a further admixture of water and may remain for weeks, or months, in contact with water without its water mixed with it being appreciably increased, the clay in the dry state sucks in water with the greatest eagerness, producing a sudden increase in volume, making innumerable cracks in the dried-together mass, breaking it up into small portions, among which the water distributes itself, easily and equally. This method of preparation for manufacturing purposes is only to be considered as exceptional as, for cheapness, it is far

inferior to the method of weathering, or we would better say, wintering. Here again we meet with an effect of water, this is in the moment when it passes over from the fluid to the solid crystalline condition and it will repay us to consider somewhat carefully the course of the operations.

Water exhibits an anomaly, as compared with all other fluids, in that it does not, like these, increase its volume on becoming warmer or decrease it on becoming colder according to a rising or falling scale, but reaches the minimum of its space at a temperature of 4° C. (39.2° F.) a further reduction of temperature causes it to expand very slowly, but on passing to the solid condition the increase in volume is very sudden and intense, so that by this peculiar property the mechanical effects are considerable, resulting in forceful action loosening and bursting of the mass that is saturated with water. The action of the freezing water would, nevertheless, be far from having its intense effect if it were not aided by another factor, consisting in this that the water, on becoming ice, makes a great effort to arrange its crystals in a certain order and shows all the peculiar properties which we know to belong to crystalline substances. We can watch the effect upon clay by the crystallization of water on its becoming ice by taking, for instance, a green, undried brick and exposing it to a low temperature. In such a piece of clay we can plainly see, with the naked eye and better still with the help of a magnifying glass, cracks which arrange themselves in the peculiar flower-like figures of ice crystals and change the brick into a heap of clay particles that are only loosely held together. These cracks are not produced by the expansion of the ice because, in such case, the expansion being regular the result would only be a break at some point which was weakened by imperfect homogeneity, but the effect has been produced by the ice crystals, which have broken up the clay to obtain the room necessary for their formation, so that they have not only loosened the mass by their increase in volume, but have created a network of fine channels, which, on the disappearance of the ice, would lay the clay open, deep into its interior, to the influence of the atmosphere.

The valuable influence which wintering exercises upon a heap of clay has always been known in practical work and it seems almost unnecessary to think of recommending it, even if, from other quarters, considerations are offered against it, founded, probably, more on suppositions than on scientific data. If the wished for results were not always obtained then the reason for this failure lay, simply, in the fact that we were not sufficiently clear as to what took place and the arrangements made in this wintering process did not agree

with our requirements. If for instance we pile up, in the autumn, a heap of clay, 10 or 15 ft. high, and expect it to be opened up by lying exposed during the winter, then we can rest assured that when the spring comes we shall find that a comparatively small portion of it has been loosened, that is the outer crust, which has been acted upon by the rain, snow and frost, while the rest of it is found to be in the same condition as it was when piled up in the fall of the year; so that we might as well have saved ourselves the labor and expense. If we wish to thoroughly succeed with the wintering process then it is absolutely necessary that the clay should not be put up in deeper layers than the frost can penetrate and by laying the earth up loosely, provision should be made for the admission of air and moisture and the formation of ice.

Many clays, particularly those that are rich in sulphides, as the aluminous earths of the lignitic formations frequently are, soon after they come into contact with the air begin to weather, they swell and then fall into small pieces. The cause of this is, in the main, the same as that which we found in the freezing of clay. Through the action of the air crystallizable salts are formed, mostly sulphate of iron, sulphate of alumina, magnesia salts and gypsum, these through their chemical combination with water acquire a larger volume, but then by the energy of crystallization, through concentration of the scattered materials upon certain points for the formation of larger crystals, a disruption of the solid mass of clay takes place in a similar manner to that which we observed in freezing.

When working the clay to a solid mass which not to be further softened by water, we again meet with the influence which the crystalline condition of individual portions exert upon its properties, though entirely differently to the ways described above. I do not think it right to pass over this matter in silence because it does not appear to have received that notice, in ceramic literature, which it deserves; I mean the influence of the temperature required for burning the clay.

By the burn, is generally understood that condition of the burned clay in which, through the action of the heat, some portions of the mass are melted to such an extent that they cement together other particles which are not fluxed, without the porous character being disturbed or any noticeable alteration be effected in the shape. If the fluid condition, caused by a high temperature, or long continued action of it, goes so far that there is enough vitreous material to fill up the pores of the clay and at the same time, to produce a noticeable softening of it, we come to the state of hard porcelain and clinker, in which, finally, all chemical differences and formations

disappear by the material taking on the condition of a glass or slag.

This process of complete burning brings about the formation of a certain small quantity of a fluid substance, which we are in the habit of considering, physically and chemically, as glass. This binding material, the chemical nature of which, here, is a matter of indifference and which is subject to great variation, is the result, partly, of the melting of certain fusible compounds present in the clay and, partly, is the result of a chemical process, which takes place during the burning, but which must never be allowed to go very far, if we wish to preserve the earthen character of the clay. The degree of heat required to attain that amount of fluxing in the clay sufficient to bind the unmelted portions together and, on cooling, to form a sufficient bond, is in the first place dependent upon the chemical nature of the materials, but also upon the state of subdivision and the physical properties of the components, particularly the silty and the sandy portions, which, as a rule, are the only things that, quantitatively considered, are taken into account and which, during the disintegration process, retain the remains of a crystalline structure.

As to the influence the crystalline structure of the silicate compounds have upon its melting point, exact scientific investigations of this subject do not yet exist, but still it would appear that the greater refractoriness possessed by some of the natural crystallized silicates, as for instance, feldspar and leucite, in which, from practical experience, it had not been supposed that the melting point was so high, the molecular attraction works against the fluxing, which must be accompanied by a complete cessation of the crystalline structure.

Even if this point is not yet decided we still have sufficient positive observations to enable us to say that the crystalline condition weakens chemical action to a marked extent and makes it slower, as is seen in the fritting of clays, so that some materials exhibit themselves as, in the highest degree indifferent to chemical action if they are in the crystalline state.

For the hard burning of porcelain it is always the most fusible portions, or those which, according to their composition and physical constitution are disposed to change at the lowest temperature, that must supply the bond and this may be either the clay, the sand or the silt, so that the changes that occur cannot be determined with certainty until each separate constituent in a certain material has been investigated and its particular properties taken into account. The value of this for giving us a knowledge of our materials must not be underestimated and will assist in throwing light upon one of

the most obscure chapters in the investigation of the properties of clays.

III.

The appearance presented by the crystalline formations in the interior of burned clay are very different to those that can be observed in the clay still moist in the bank and we can find an analogy that we became acquainted with in the freezing and for this reason that an exertion of force taking place in the interior mass of natural moist clay, through the formation of crystals, only causes an alteration in shape and an increase of density, without disturbing the continuity of the mass, while in the rigid condition of the dried, frozen and burned clay it always exhibits itself by a loosening and breakage of the material. The substances which, by their crystallization in burned clay bodies, produce disruptive effects through bursting and scaling off are caused either by insufficient burning and consequent non-vitrification, by absolute salts already in the clay or that are a product of a secondary weathering, or else they have been accidentally introduced, as in bricks for instance, by water containing lime or by that used when laying the bricks in the wall; they are, mostly, sulphates, nitrates and carbonates and chlorine compounds with the alkalies. lime and magnesia. The effect which with the help of water their varying transpositions and depositions have within the burned clay are very similar and although the common explanation of these appearances has been to attribute them to saltpetre it must be stated that, in the greater number of such cases, no trace of saltpetre or nitrate salts can be found and that precisely similar appearances can be produced by any soluble salt that, from any cause, has obtained admission to the pores of the clay. Actual saltpetre (nitrate) formations can only be produced where the clay is at the same time a suitable soil for the propagation of the lower vegetable organisms, fungi, molds and infusoria.

As we saw was the case in the deposition of clay, water, here also, plays the part of intermediary for the transposition of the crystallizable substances, and here, too, if we follow the principal course of the water channels we can easily find the places where the greatest effects are concentrated. If we observe a piece of burned clay, for instance a common brick, at a broken part, we shall see in most cases that the material is not equally distributed, but that some parts, by their color, porosity and grain, show that they differ from others. Let us go further and examine the fracture of the brick with a magnifying glass we shall find that in consequence of the unequal shrinkage during drying and burning, of the differing parts, particularly around small stones and the coarser grains of sand and

the dividing lines caused by silty and clayey portions, breaks and fine cracks are to be seen, which weaken the cohesion of the brick, the close union of its parts.

The fluid which produces the movement of the crystallizable salts in the interior of the stone is set in motion, principally, by evaporation; this takes place, to the greatest extent, near the surface of the brick, while in the interior evaporation is entirely absent or is very limited. By capillary attraction within the porous mass the fluid is sucked from the inside to the surface and in this way a circulation of the water is set up, which, on the entrance of water from the outside, travels in the reverse direction, carrying with it all the salts dissolved in it. The circulation of the water is, naturally, the most active in those places where it meets with the least resistance, that is, in the cracks and fissures, the places from which it is easiest for further disintegration to start and which, at the same time, offer the most favorable positions for the depositions of crystals because there is room for their symmetrical formation. If outgrowths of crystalline salts have once formed at such points then the further crystalline process seeks to increase some of the individual crystals at the expense of the others so that, on any new supply of water coming in, the smaller crystals are more readily dissolved than the larger ones and on the evaporation of any part of the solvent the re-formation of crystals takes place more readily than if they had to find new crystallization points. The result of such a collection of crystalline substance at certain favorable points necessitating space for the formation of the crystals and exerting pressure upon the surrounding mass of clay can never have a similar effect to that which it has upon the moist clay, leading, merely, to a movement of the material and an alteration in its structure, but in the burned clay it can only produce breaks, spalling, "molting," or cracking; the more so that it is only in exceptional instances that the material is able to offer sufficient resistance to the pressure exerted within it. It seems, therefore, clear that what is variously called "petreing" efflorescence, whitewashing, or scum, is more likely to be found on material where, through insufficient burning, the salts have not been destroyed or evaporated and the material itself has not reached that degree of solidity and resistance to disintegration which we have a right to demand in a good building material. But even in a brick that, outwardly and from a superficial examination, seems good, destruction is certain to result if the formation of crystals is favored by the easy circulation of water, that is to say, if the structure of the brick is not in the highest possible degree homogeneous.

A homogeneous brick will not, naturally, be able to withstand

forever, the crystalline formations continually seeking new points of attack, but it is capable of offering an incomparably longer resistance than one with defects in its homogenous character, one in which during drying and burning, unequal contraction and weakening of cohesion have occurred and in whose weakest places the destructive forces can concentrate.

Defects in the Investigation of Brick Clay.

The recent investigation by Bischof and Richters for the purpose of determining the degree of refractoriness of fire clay have thrown some light upon this difficult subject, but they have, apparently, placed all scientific observations in complete contradiction to practical knowledge in proving that the melting points of clays depend, according to exact and well defined laws, upon their composition and it cannot be denied that valuable service has been rendered by these labors, not only to the ceramic industries in general, but, in even a greater degree, to those industries which employ fire clays as materials of construction in their plants, that is to say, those which need a very high degree of heat for their manipulations. The question forces itself upon us, to what extent these investigations may usefully apply to other divisions of the ceramic industries and hereupon we are compelled to admit that the conclusions to be drawn from them are not of such kind that they may be applied without further consideration, and it looks as if the possibilities of their application have, perhaps, been very much overestimated.

The position to be assigned to fire clays, which have to be used as building materials enclosing a space where an extremely high temperature is produced, is very different from that of such products as have only to be subjected once to the action of intense heat. These latter are fine and coarse pottery, bricks, tile, etc. In the first case a change in the chemical and physical properties always accompanied by a very undesirable change in shape, is to be avoided as much as possible, while the other products, which have to withstand the influence of the elements, should undergo a certain amount of change. The requirements are, therefore, different for these different materials, and while for the production of pottery the action and reaction of the materials should result in the highest degree of homogeneousness in every part, for the production of highly refractory construction material such as fire brick, it is desirable to have a certain degree of non-homogeneousness, for this will, at least, hinder the chemical action of the clay particles upon each other, the final result of which can only be a melting of the material.

In order that there may not be any misunderstanding upon this point, it will be necessary to consider it carefully.

Clay, as I have repeatedly shown, is not a homogeneous substance, in the chemical sense of the word; it is not even a substance of which the most minute particles can be regarded as similar; on the contrary, it is a mixture of different bodies, each possessing definite physical properties and it can only be considered as homogeneous to just the extent that the various bodies, lying side by side, will permit. If the clay, under certain conditions and upon a superficial examination with the naked eye appears to us to be equal throughout, upon looking at it through a magnifying glass we will always be able to distinguish in the mass of clay such varying particles as of mica, grains of sand, lime and the shells of low organisms. Although it is not very noticeable it can be seen that the material is not homogeneous. The condition of absolute homogeneity is not found until the clay, under the influence of heat, is melted to a glass.

This degree of homogeneity, the result of bringing the clay to a fluid state, is never sought for at all in fire brick, and only to a certain point in pottery. In this it should go so far as it can without deforming it. What is required is not a completely fluid condition of the entire mass of clay, but that only a portion of it shall be affected. The sole object of preparing the clay and rendering it homogeneous is to distribute the fusible particles equally throughout the entire mass.

When producing highly refractory material we intentionally give it a certain degree of non-homogeneity, by giving the mass of material as few points of contact within itself as possible, as it is from these that the melting starts. In this way we produce a physical condition which offers a certain resistance to fluxing.

Clays that have to withstand the higher degree of temperature differ greatly, both chemically and physically, from those which are used for pottery. In the first case we have to do with a mass that is comparatively purer and more uniform and has for its main constituents only a definite combination of alumina, silica and fluxing material, which offer greater or less chances of high refractoriness, according to the relationships in which the component parts stand to each other, while the actual reducing materials (sand or calcine) are either quantitatively of small importance or else they partake of the refractory character of the principal mass.

For the production of pottery, bricks and all such articles as have to be burned so as to offer resistance to the action of atmosphere and moisture, we always seek for some difference in the fusi-

bilities of the component parts, so that one of the components will not be affected by the heat to which the object is submitted and thus in a measure acts as a skeleton, enabling the object to keep its shape unchanged, while the other components melt, flow around and, on cooling or setting, completely protect the unfluxed portion from the influence of the atmospheric elements.

For refractory materials which have to suffer a great and continued heat, we require some degree of uniformity in the refractoriness of each constituent, but for other kinds of clays we need a comparatively low melting point for some of the components, while the others should be much more inert under the action of heat.

If we contrast, in their chemical and physical properties, the two kinds of clay, those for building materials, which have to be capable of offering the greatest possible resistance to the action of fire on the one hand and of water on the other, that is to say, the plastic refractory clays, with the brick clays, then we can classify them as follows:

Plastic clays consist, principally, of the weathered, or disintegration product of a certain mineral or rock. The clays have varying quantitative composition, depending upon the formation of the original mineral, but always having, in the main, the peculiar combination of alumina and silica, which we call clay substance, while other, detrimental, substances, are less noticeable and do not have much effect upon the properties of the clay, but it is quite different with the brick clays. These also possess, in greater or less degree, their clay substance, which gives to them the characteristic of plasticity, but the clay substance is mixed to such an extent with the debris of rocks, such as silt and sand and this debris does not even come from one and the same mineral as the clay substance does. Those non-plastic substances, even if they are not always present in greater quantities than the clay substance itself, are still in sufficient abundance to have a very marked effect upon the properties of the whole material.

After chemical analysis has shown the relations between the alumina, silica and fluxes and that these separately belong, principally, to a single, well defined, combination, we are able to draw our conclusions as to the degree of refractoriness of the material. We do this by means of the laws that have been formulated by Bischof and Richters, and we do this with more or less accuracy according to the greater or less degree of purity in which the substances are formed. If, however, we were to proceed in a similar manner with brick clays, we would obtain theoretical data differing so greatly from the practical results that they would have no value

whatever for giving us information respecting our material. The general chemical analysis only gives us an average value of the composition of those constituents which make up the clay and which, in their chemical formation and physical properties differ so much from each other. As the clay, after burning, retains its earthen character and the various constituents only react superficially upon each other, the chemical analysis gives us absolutely no standpoint from which to determine the properties of the whole.

It is possible for two brickclays to have exactly similar chemical compositions and, notwithstanding, to differ from each other in every respect, because the general analysis offers no conclusions whatever as what proportions of the silica, alumina and fluxes fall to the clay substance, the silt or the sand. For instance, it may be that in one case the whole, or at least the greater part, of the fluxing substances may fall to the clay substance, in another case it may be the substances with reduced plasticity. In this way the materials, though showing similar percentage compositions, will entirely differ the one from the other. In the one case it may be the clay, in the other the silt or sand, which though otherwise similarly combined, forms the easier fluxing component, or there may be accessories such as admixtures of iron oxides, or lime carbonates which, according to the way they are distributed, among the clay substance, the silt, or the sand, are inclined to exercise a powerful influence, thereby producing a number of variations for which a mere chemical analysis can offer no explanation.

If from this it should appear that chemical analysis has an extremely limited value for the purpose of giving information respecting the properties of a brick clay, this would be, in the highest degree, a one sided and inappropriate conclusion. In any employment of the clay where it entirely loses its earthen character, such as the manufacture of portland cement or of glass, the chemical condition is of the first importance and the other, physical, properties are only of consequence in the degree and measure that they are able to hinder the destruction of the earthen character of the material. Here it is that the chemical analysis enables us to form a definite conclusion, but for our work it is the physical properties that are of the first importance for enabling us to judge the clay and the chemicals are only of value in so far as they extend our knowledge of the physical conditions. In this case, to put it concisely, the duty of the chemical analysis will be to determine the chemical condition of the physically equivalent constituents, such as the clay, silt, sand, etc., separately and individually and enabling us to compare them with each other. In this way we can secure definite data

respecting the component parts while a similar analysis applied to the whole would completely mislead us.

We find herewith indicated the necessity of a mechanical analysis of our clay, along with, or much more, before, the chemical, when the examination is of a material for pottery and especially for brick manufacture and although the importance of mechanical and physical investigations have been repeatedly insisted upon by scientific men, the work has not, hitherto, been carried out with sufficient stringency to enable the results of the investigations to be of any real value to the brick industry.

If we look at the analyses of clays, whether pottery or brick clays, such as we find in many chemical and technical books, we shall see that they are, in most cases, a summary of the component parts, silica, alumina, lime, iron oxide, etc., stated in percentages or, at least, along with the analysis of the slummed material—that is to say, of the clay substance in the purest condition in which it can be obtained—it is stated that besides this there is so and so much per cent of dust and fine sand.

When examining a very pure clay where the percentage of plasticity reducing material is small, this may, perhaps, suffice, but when the clay contains 60, or more, per cent of sand—as I have frequently seen in clay analyses—without any indication being given of what this sand consists of, what influence it may have upon the properties of these, or what its own physical and mineralogical properties are, we must consider this as a serious defect. The value of such an investigation is reduced to zero and it only deserves to be regarded in the light of an exercise in analyzing.

Such investigations will only have a real, practical value for the ceramic industries when we accustom ourselves to regard a clay, even when it is brought to the highest state of homogeneity by mechanical means as a heap, an assembling of particles lying alongside each other, but differing in kind, which are independent of any definite chemical composition. The physical properties of the whole give it its characteristics, which make it possible to employ it in a certain manner, whereby the changes effected by the process of burning do not apply to all the particles alike, but only to some of them which are peculiarly disposed to change, while with the others an attachment, at most, should take place at their points of contact. If we push the action of the fire further than this point we shall not get what we seek, but instead of an object in which vitrification has only commenced and which has not lost its earthen character, we get a complete glass from which the earthen character has entirely disappeared.

I think that in the foregoing I have made it sufficiently clear in what direction we must make our investigations of impure clays, such as brick clays, if we wish to reach conclusions at least approximately as correct as the results that Bischof and Richters in their investigations of fire clays succeeded in getting with their comparatively very pure clays. It will only be necessary to very sharply separate the constituents that are unequal in kind and in value, so far as the methods of science will permit and treat each of these as of equal importance. It is, in fact difficult to understand why, in all the analyses, even when a separation is made, the entire attention is devoted to the plastic clay substance, while the non-plastic portions are treated as though they explain themselves. But are we not compelled to attach as much weight to these given and necessary factors as those? Or is it to be supposed that the non-plastic portions of the clay did not exhibit as great varieties of qualities as does the plastic?

The preliminary work for such a thorough investigation of a clay is provided by the mechanical and the slumming analysis which, by means of a series of comparative results supply just as definite laws for the classification of brick clays as those evolved by Bischof and Richters, although these will be much more complicated. If the mechanical and the slumming methods of analysis have, up to the present time, occupied a very low rank in the investigations of the properties of clays, the reason for this is that the methods employed were so faulty and the results exhibited so many discrepancies that they were, with perfect justice, regarded as of very little value.

However insufficient may have been this separation of the substances that were, physically, entirely different from those which were approximately similar, the methods, if more extensively used, would have thrown considerable light upon the real constitution of the clay, but the great number of chemical analyses that have been made have not carried us one step further. The Schoene's slumming test apparatus, which gives us an incomparably more accurate and more convenient means of separation than was hitherto possible, is an invaluable gift by science to the clay industries.

It is, however, not only the chemical investigation of each constituent separately that is so important for our knowledge of a clay; it is, perhaps, in yet greater degree the mechanical analysis. The knowledge of the structure of the clay, the average size of the grains of sand, their shape, or formation, whether round, ground, or split, that is, showing cleavage surfaces, or whether they are in

scales (lamellae), the degree of cohesion; the plasticity of the clay; the extent of shrinkage in drying and in burning; its porosity and capacity for holding water; its hygroscopic properties; the presence of foreign bodies in the clay, their appearance and the way in which they are embedded in it; all these are questions to which chemical analyses can give no answer whatever and yet these are of as great, probably of greater, importance than a knowledge of the chemical composition. These questions can only be solved by careful scrutiny in the claypit and the most subtle observation, with the aid of the microscope, the balance and the slumping apparatus. They offer a multiplicity of aspects necessitating deep study to enable us to find satisfactory solutions.

I am convinced that these questions are of prime importance for everyone interested in brick manufacture, in order to explain the multiplicity of the phenomena met with in the preparation and working of clays. If these are neglected then all other scientific investigations will be useless; we know nothing about the relationship between the degree of moisture in the clay and its shrinkage and cracking; nothing about the interdependence of size of grain and quantity of reducing material and the porosity and power to hold water. It will require many years of painstaking investigation and zealous study in this, which has hitherto been completely neglected, before results are obtained which will be satisfactory in practice.

It is far from my intention to offer a reproach to science because this field—so far as the clay industries are concerned—has been left entirely uncultivated; I do not even make it answerable for the undeniable deficiencies. As we see in so many industries that know how to make use of the powers of knowledge, scientific investigations are of practical value only where they are not undertaken for themselves alone, but in answer to questions put by the industry and with a fixed object. If the clay industries have, up to recent times, failed to come forward with such questions and only now is beginning to venture, very timidly, in this direction, the reason is that they did not themselves know what they were in need of.

It is not my purpose here to attempt to fill the voids in these investigations of our clays, but only to incite the practical workman to the endeavor to state with precision what he needs to know, so that a few investigations, carried out with the necessary many-sidedness will be of far greater use and throw immeasurably more light upon the questions that are of such importance to the clay industries than all the many half and one-sided investigations which we already possess.

The Mechanical Analysis of Clay.

It was shown, in the preceding article, how insufficient a mere chemical analysis is for giving a knowledge of the properties of clays, unless this analysis is based upon a preliminary separation of the dissimilar constituents of the clay by means of a mechanical analysis. The admirable work of W. Schutze has taught us how to make this separation and how it is quite in our power, within certain limits, to do this with scientific exactness. Ignoring the physical properties of clays has been the principal reason why science has given us so little assistance in the clay industries; indeed chemical analyses have led to conclusions which were in direct contradiction to practical experience, and if these deficiencies cannot be made good at once, the cause is that comparatively a small number of, approximately, exact analyses are available and the most of even these are incomplete. In the nature of the chemical analyses, which could not be treated mathematically on the basis of the few existing examinations, it will be necessary to make a large number of these from which the laws governing the matter may be evolved.

If, in the following, I give some examples of slum analyses, this is not done with the idea that any far-reaching results will be got from them, which can only be obtained from a great number of investigations; my sole object in this is to firmly establish definite conceptions of such constituents of a clay as differ notably from each other in their physical properties.

We are accustomed to regard as clay substances, these particles which are found in the greatest possible condition of decomposition, where the extraordinary superficial extension produces the peculiar phenomenon of attraction of surfaces which we call plasticity. These very strongly exhibit all the peculiarities which we see in clay, using the word clay in its ordinary acceptation.

The actual clay substance—although taken in the strictest sense of the word, it may not form the entire body of the material—is that portion which is easiest slummed out of the clay and remains suspended the longest in the water. As all our apparatus are more or less imperfect and as, in nature, there is no jump from the finest condition to the coarsest, but instead of that we find all possible gradations, we must agree upon the manner of making those which are necessary for our purpose. In the future treatment of this subject "clay substance" will be noted as that which, in the Schoene slumming test—the nearest perfect apparatus for the purpose at present in existence—is carried away by a stream of water having the lowest velocity that can be determined with certainty. This is a current velocity of 0.18 mm. per second at a pressure-height, in

the piezometer, of 20 mm. According to the circulations made by Schoene of the velocity of free fall in water of particles of quartz and also according to the direct microscopical measurements of the slummed products from his apparatus at this current velocity, the maximum size of the grains is 0.010 mm.

What, at this lowest current velocity, is not separated from the clay, still shows differences in its properties from the actual clay substances. I have, in agreement with what has been done elsewhere, noted this as silt. This consists of minute mineral detritus, so fine that, rubbed between the fingers, it produces a slippery sensation; mixed with water it gives us a mass, which can be modeled, but in short and which on drying has but very little cohesion. When rubbed with the finger nail it remains matt, while clay substance, treated in the same way, becomes brightly polished.

Under the title "silt" will come all materials of which the size of the grains are from 0.010 to 0.025 mm. at a current velocity of 0.70 mm. per seconds.

The succeeding coarser particles are to be considered as sand dust, for although this material is, physically, of a sandy character, the sense of touch can scarcely recognize it as such. The sand dust represents a current velocity of 1.5 mm. per second, with 900 mm. pressure height of the piezometer and the sizes of the grains are from 0.025 to 0.040 mm.

We distinguish as fine sand the grains measuring 0.333 mm. and as coarse sand everything above this size.

The clays which were examined differed considerably from each other in their properties. The one marked a. is an extremely fat and plastic fireclay from the lignitic formation at Senftenberg, Lausitz. It is of a gray-white color. Clay b. is from the same place and is found in alternate layers along with a. It is remarkable for its extreme fineness as well as for its leanness and shortness. That marked c. is a fireclay from Grenzhausen in Nassau; it is used, without any addition or preparation, for the manufactures of the "Kannebaecker Land," which are so highly esteemed on account of their durability. Finally d. is a clay that is found between the loam strata on the north border of Berlin, near the Schoenhauser gate, it alternates with iron-shot clay, is fat and has sharp sand. It is very strong in drying and shrinks and cracks very much.

The above characterizations find their expression in the showing of the slumming analyses.

The four clays; a. from Senftenberg, fat; b. from Senftenberg, short; c. from Grenzhausen, and d. from Berlin, gave:

| | a. | b. | c. | d. |
|---|--------------|-------------|-------------|-------------|
| | Per ct. | Per ct. | Per ct. | Per ct. |
| Coarse sand, size of grains above 0.333 mm. | 0.58 | 0.34 | 0.18 | 21.20 |
| Fine sand, 0.333 to 0.040 mm..... | 3.00 | 28.46 | 10.64 | 11.58 |
| Sand dust from 0.040 to 0.025 mm... | 3.52 | 13.84 | 9.08 | 14.84 |
| Silt from 0.025 to 0.010 mm..... | 11.16 | 20.24 | 10.88 | 2.14 |
| Clay substance 0.010 to 0.000 mm... | 82.18 | 37.10 | 68.32 | 62.00 |
| | <hr/> 100.44 | <hr/> 99.98 | <hr/> 99.10 | <hr/> 98.76 |

A comparison of the figures given above assist us in drawing some conclusions as to the properties of the materials. While in the most plastic of these clays, that marked a. from Senftenberg, shows the greatest proportion of clay substance, in addition to this there is hardly anything but the finest mineral detritus. The other clays show more of the finer and finest non-plastic constituents and give the clays a less plastic or short character, but without depriving them of their essential properties of fineness and capability of being formed and modeled. In the Berlin clay, along with the plastic mass the relatively coarser and non-plastic portions are prominent, while the finer portions almost disappear. In this case we find properties which are not altogether desirable.

There is no doubt that it is only the variation in the constituents of a clay through the size of the grains, their shape, the formation of their surfaces and the mutual relationship of these things, which produce those differences that make it so unendingly difficult to form a correct judgment upon the material. So long as exhaustive and systematic investigations in this direction are not made, which will enable us, from a large number of observations, to draw reliable conclusions, the phenomena of shrinkage, cracking, porosity, capacity for retaining and for taking up water, will remain unexplained and in our practice we shall be compelled, in the future as in the past, to grope in the dark. Unfortunately the number of investigations at present available is so extremely small that they can offer us little of practical value until they are supported and extended by a considerable increase in their number.

The Chemical Constitution of Clays.

Although the data furnished by the physical investigation of clays are valuable as to their behavior when worked in the wet state, when drying and when burned at a low heat and though the chemical analysis is so useful to manufacturers for determining those injurious constituents which, according to Bischof and Richter, affect the degree of fusibility, all these are not sufficient in every case to

sharply characterize the clay, or body of which clay ware is to be made and it happens, often enough, that the scientific deductions and the results arrived at in practice, are more or less wide apart. It is therefore necessary, in many cases, to verify or to extend the scientific verdict by practical tests so as to make them applicable to manufacturing. The reason for this lies in the fact that the physical and chemical analyses do not show much mutual relationship and also do not give us conclusions respecting all the conditions. The physical analysis teaches us the relationship between the clay substance and the non-disintegrated mineral detritus of various grain-sizes and gives us conclusions respecting a series of phenomena, which are more or less independent of the chemical composition; but the chemical analysis gives us next to no information at all as to the physical properties of the clay, and will only admit of our forming conclusions upon the assumption that all the components, whose presence is shown by the chemical analysis, will come into operation. This is very far from being at all times the case, particularly when the clay includes within itself coarser portions; in such cases as these the results of the chemical analysis should always be checked by suitable tests in practical work for even the two methods of investigation together are not sufficient to give us full information as to the character of a clay.

This apparent contradiction between the results of scientific investigations and those of practice has been very clearly shown by the attempts made at one time at Sevres to get at the secret of hard Chinese porcelain by means of chemical analysis. Brongniart records that the attempts to produce porcelain by bringing together their separate constituents—silica, alumina, alkalies, etc.—as found by chemical analyses, when burned in the porcelain or sharp fire, did not make a porcelain at all, but only a white enamel. It follows from this that not only are the chemical constituents, according to their quality and quantity, of influence upon the properties of a clay, but that the combinations among these constituents, which are already completely formed within the mass, are of importance for the character of the whole.

We may, in general, consider clay as a mixture of grains of quartz; of unweathered or non-disintegrated mineral detritus and of the disintegration product of the latter, the clay substance; this clay substance is, mostly, a hydrated silicate of alumina. As the unweathered mineral detritus and the clay substance may differ very considerably, not only qualitatively but quantitatively, and may show striking variations in the sizes of their grains, it is obvious that there can be no question of an exact knowledge of the clay until we

succeed in determining these similar constituents according to their kind and amount in the mass.

We know more about the internal constitution of the clays used for the higher branches of the clay industries, because the raw materials are the purest that can be obtained and they are, to some extent, chemically well defined.

A body for hard porcelain is generally made of three things; quartz, feldspar and kaolin. The quartz consists practically of crystalline silica; the feldspar is a combination of silica, alumina and alkalies (potash and soda; sometimes partially replaced by lime and magnesia), the kaolin consists of similar constituents in other conditions and combined with water, but with, mostly, only insignificant quantities of alkalies. The water is not taken any account of in the chemical composition of the clay. If we know the chemical composition of the constituents of a porcelain body—that is, the quartz, feldspar and kaolin—and wish to compose a porcelain of a definite elementary composition then, as these three have one or more elements common to them all, we may often vary them without the percentage composition of the mixture showing any great difference. Notwithstanding this, the properties of the mass and those of one or two of the closely allied components of the mass may differ greatly, according as these are more in evidence and that, too, in spite of their being chemically alike. In practice, materials are never employed the composition of which is such that they can be regarded as single and pure chemical compounds. This may be the case with quartz (or pulverized flint) and with feldspar, but never with kaolin, which, even when slumped in the most thorough manner, always shows more or less proportions of the original rock, such as quartz and feldspar detritus, which have escaped the disintegration process. As the materials to form a porcelain body are put together empirically and the quartz and feldspar contained in the kaolin are unknown and could not be directly deduced from the analysis by the analytical methods heretofore employed, the conditions, whenever the source of the raw material is changed, made a new mixing necessary and, very often, new trials as well. This would not be necessary if the relationship between the quartz, feldspar and actual clay substance in the kaolin could be determined. For those branches of the ceramic industries which make their body or mass out of raw materials whose properties do not change and that are obtained from certain known sources, it is not difficult to make a change, empirically, in the mixing, the properties of the mass may too be varied within certain limits; but it is very much more difficult in those industries where the raw materials that have to be used

are of much less marked individuality; plastic clays, potter's clays, brick earths, which, too, by nature's slumming process, have taken up foreign bodies, substances that do not belong to the original disintegration product and which, lying in the bank or pit near or above one another, exhibit great differences in character. Clays of the first kind, it is true, demand a greater amount of skilled labor, but it cannot be denied that the latter gives much more trouble in manufacturing and I have heard a competent ceramist declare that he found it much easier to produce a white and faultless porcelain or a stoneware than a terra cotta or a brick of a required color that would at the same time be weather-proof, the moment it became necessary to make any change in the natural raw material and employ raw materials from another source, with the characteristics of which he was not fully acquainted.

These difficulties, caused by our ignorance, in the one or the other direction, of the properties of the raw materials to be employed can, as a rule, only be overcome by empirical trials, which cost much time and money, besides disturbing the regular course of manufacturing. These difficulties would be greatly diminished by our possessing a better knowledge of the internal structure of the clay and by knowing how the constituents, which the chemical analysis shows to be present, are distributed among the portions of clay similar to each other, but which in their chemical and physical properties show constantly recurring differences, of those that do not disintegrate and that resist all chemical influences except at the highest temperatures; of the quartz, which is reckoned with the disintegratable materials, the mineral detritus—feldspar, etc.—and of the actual clay substance in the widest sense of the word, which clay substance is the product of disintegration of all the minerals that contain materials for forming clay.

Such a better knowledge of the more closely allied portions of clay has been sought after during a long series of years by several investigators, and has found its expression in the so-called rational analysis of clays; this is based upon the varying comportment, chemically, of the different mineralogical constituents of clay, but its chief application has been to the investigation of the actual clay substance, while the other substances with the exception of the free amorphous silica, have not received the attention that they deserve. A consideration of these appears the more desirable for the clay industries, inasmuch as these substances, which from their physical properties cannot be regarded as clays, form a noticeable percentage even in the purest clay, that is in slummed kaolin, as

well as in fat, plastic clays; in the impure clays and the brick earths they mostly form more than half the contents.

A series of porcelain earths and plastic clays have been examined in accordance with the methods used by Forschhammer and Fresenius and the results have been published for the purpose of throwing some light upon what takes place when feldspar weathers to clay. The analytical method is based upon the fact that the disintegration product of the feldspar, which is the actual clay, is completely decomposed by boiling sulphuric acid, while quartz, feldspar and other minerals rich in silica are not affected by it. In addition to these analyses we find in our literature a number of others where the actual clay substance is given along with the free silica and those components that are soluble in hydrochloric acid; the undecomposed mineral detritus is simply denoted as "insoluble residue" without any indication of what it consists of. Other analysts have employed the Forschhammer and Fresenius methods to determine the different conditions in which silicas are found in all clays and exhibit different properties, such as chemically combined silica; as the amorphous silica result of weathering in the open (in air) or as crystalline silica (quartz sand). Among these analysts are Bischof and Richters, whom we have to thank for a large number of carefully conducted analyses of clays. In these analyses that portion of the clay which is insoluble in sulphuric acid is to be regarded simply as quartz sand and is set down as free crystalline silica. This method of determining the amount of silica can only be admitted in those cases where the clay consists of clay substance and quartz and does not contain other minerals that cannot be decomposed by sulphuric acid. As the analyses which will be given later on will show, the insoluble residue remaining after dissolving the clay substance in sulphuric acid and which some analysts denote as quartz are, in most cases, not pure silicas; on the contrary they usually contain appreciable quantities of alumina and alkalis, which give them the character of a mixture of quartz and alumina silicates.

In an earlier discussion of the various methods of analyzing clays and of the conclusions to be drawn from them, Aron pointed out the great importance for practical use of the rational analysis in addition to the chemical and physical analyses. The rational analysis had, hitherto, been employed only for the purposes of pure science. This attracted attention to the method and not only in the direction of determining the quantity and composition of the clay substance, but also the mutual relationship of the quartz to the undecomposed feldspar and other minerals, so as to throw some light upon the question in this direction as well.

Before such an examination of a series of clays is undertaken, the method itself should be tested, to find whether and under what conditions it is capable of making a complete decomposition and separation of the clay substance from the undecomposed mineral detritus. To this end clays of very different chemical and physical composition were selected and submitted to the action of sulphuric acid, the time being noted of the production of the residues. In other words, when the reaction could be considered as complete. For this purpose the extremely fat pottery clay of Gruenstadt and the very "short" brick earth of Schwarzeuhette, near Osterode in the Harz, were selected.

Of each of these clays, three samples of about 2 gr. weight each were taken. A sample was put into a platinum crucible with water and boiled until it was completely broken up; to this was added 10 ccm. of concentrated sulphuric acid; the water was then completely evaporated, first on the water bath, then over the direct fire, and the action of the sulphuric acid continued for five to six hours; the temperature being maintained just below the boiling point of the acid, about 300° C. With the one sample nothing more was done, the dried residue of the second sample was rubbed up with concentrated sulphuric acid to a thin slum and again subjected, for about five or six hours, to a temperature of about 300° C.; with the third sample this operation was repeated a third time, so that the times during which the sulphuric acid acted upon the samples of clay were, respectively, 5 to 6, 10 to 12, and 15 to 18 hours. Thereupon the samples were first boiled out with water, then twice, alternately, with dilute caustic soda and dilute hydrochloric acid in order to remove the sulphates that had been formed, the separated silica was boiled out, the sandy residue was brought onto a filter, washed, incinerated and weighed.

The following table shows the quantities of residue obtained:

| Time of Action of Sulphuric Acid. | 5 to 6 hrs. per cent. | 10 to 12 hrs. per cent. | 15 to 18 hrs. per cent. |
|-----------------------------------|--------------------------|----------------------------|----------------------------|
| Gruenstadt clay | 8.64 | 7.79 | 7.69 |
| Brick earth from Schwarzeuhette | 76.41 | 66.71 | 66.86 |

We can see from this that upon the second treatment with concentrated sulphuric acid, its action being continued for 10 to 15 hours, the decomposition of the clay substance may be considered as complete, but that the single operation, from 5 to 6 hours, seems insufficient. In order to be certain in every case, the succeeding operations were extended to 15—18 hours; that is, the product of the action of concentrated sulphuric acid was twice repeated, the residue being each time rubbed up into a thin slum with the acid.

In order to determine whether the residue really consisted of quartz alone, or whether it contained other minerals, it was digested for a considerable time with a small quantity of dilute sulphuric acid and hydrofluoric acid, the superfluous hydrofluoric acid, the fluosilicate and sulphuric acid are driven off; the remainder, consisting of sulphate of alumina and alkaline sulphates, is weighed. This was: In the Gruenstadt clay, 0.26%, in the brick earth, from Schwarzhuetten, 8.54%.

We see from this that while the remainder from the one clay actually consisted of quartz powder alone—as is assumed in most clay analyses without further investigation, the other contains quantities, which cannot be considered insignificant, of basic material, as well as other minerals that are undecomposable by sulphuric acid and which, in the fire, would make quite a different showing to quartz.

Some crystals of feldspar, which showed no signs of being weathered, were crushed and the powder treated in the same way that the two clays were, and gave a residue of 97.76%. The very slight action of the sulphuric acid is practically of no importance, it is quite possible that it may be attributed to an imperceptible weathering of the crystals, so that feldspar, under the conditions stated, may be considered as proof against sulphuric acid.

Those clays which owe their existence to the disintegration of feldspathic rocks and upon which nature has not worked any slumming process, may mostly be assumed to contain larger or smaller quantities of unweathered feldspar along with the clay substance and quartz; in all secondary deposits, that is, clays that have been moved from the place of their original formation, other substances will, in most cases, be found added. It would, therefore, be of the highest value, not only for scientific but for practical purposes, to possess some direct method that would enable us to determine, at least approximately, the quantity of undecomposed rock, in addition to the quartz, and to clearly show its composition. Unfortunately such a method does not exist and I have been unable to determine the quartz and feldspar side by side, even in an approximately correct manner, except by the indirect way through the determination of the silica and alumina.

An attempt was made to effect a direct separation of the quartz from possible silicates by melting the quartz and pure pulverized feldspar with boracic acid, glacial phosphoric acid and phosphor salts; on doing this it was found that, on the one hand, the quartz was dissolved in not inconsiderable quantities by the fiery flux, on the other, that the decomposition of the feldspar even after very

long action, was very incomplete. In consequence of this the attempt to make a direct chemical separation of the quartz from other mineral detritus had to be given up and the composition of the residue that was insoluble in sulphuric acid had to be found in the following way: It was opened up with four times its weight of sodium—potassium carbonate (where there is a high percentage of silica this is easily done without preliminary pulverizing, therefore, without any loss of material). The melting was dissolved in water, the silica completely separated by hydrochloric acid and evaporation; after filtering off the silica the alumina—which, in impure clays, often contains iron—is separated by precipitating twice with ammonia, the remainder is reckoned as alkalies.

If we are certain that what we have before us is only quartz and feldspar then a determination of both these can be made with scientific accuracy, but not when other minerals are present; nevertheless we shall get a sufficiently accurate determination for practical purposes if, for such mineral detritus found in the clay, we calculate the amount of silica as being equal to that in the feldspar.

In all future analyses, therefore, the quantity of mineral detritus, beyond the contents of clay substance, is calculated as originating only from feldspar.

(According to a later proposal made by Dr. Lindhorst in Thonind, Ztg. 1878. 2. 435., the residue insoluble in sulphuric acid is reduced by hydrofluoric acid, whereby a quantitative determination of the potash and soda in the unweathered rock becomes possible. This method was adopted by Seger and is at present, probably, the only one in use.)

I.

The following analyses of kaolins carried out in this way and presented along with a porcelain body used at the Royal Porcelain Works, Berlin, will clearly show the practical importance of this method of analysis.

The analyses made were:

1. A slummed kaolin from Ledez, near Pilsen.
2. A slummed kaolin from Kottiken, near Pilsen.
3. Porcelain body from the Royal Porcelain Works, Berlin.

| This gave | 1. | | 2. | | 3. | |
|------------------|--------|-----------------------------|-------|-----------------------------|-------|-----------------------------|
| | Total | Insoluble in Sulphuric acid | Total | Insoluble in Sulphuric acid | Total | Insoluble in Sulphuric acid |
| Silica | 49.16 | 9.05 | 49.91 | 10.65 | 63.07 | 38.09 |
| Alumina | 36.73 | 1.70 | 35.99 | 1.21 | 24.67 | 4.15 |
| Iron Oxide | 0.81 | | 0.63 | | 0.59 | |
| Lime | Trace | | 0.00 | | 0.00 | |
| Magnesia | 0.18 | | 0.30 | | 0.40 | |
| Potash | 1.18 | 0.99 | 0.76 | 0.73 | 4.25 | 2.84 |
| Water | 12.41 | | 12.34 | | 7.00 | |
| | 100.50 | 11.74 | 99.93 | 12.59 | 99.98 | 45.08 |

These figures do not, at first sight, admit of any comparison with one another and nothing indicates that we have to do here with a mixture of similar matter—quartz, feldspar and clay substance—only in different combining proportions. If, on the one hand, we calculate the relative quartz and feldspar, in the residue insoluble in sulphuric acid (each 1% of alumina corresponds to 3.51% silica of the feldspar), and on the other hand, the composition of the actual clay substance, the analysis will become very much more intelligible.

| Contents | 1. Kaolin from Ledez. | | 2. Kaolin from Kottiken. | | 3. Porcelain body Berlin. | |
|-------------------------|-----------------------|---------|--------------------------|---------|---------------------------|---------|
| Quartz | 5.08 | | 6.40 | | 23.52 | |
| Feldspathic residue .. | 8.65 | | 6.19 | | 21.56 | |
| Clay substance | 86.27 | | 87.41 | | 54.92 | |
| | 100.00 | | 100.00 | | 100.00 | |
| Clay substance contains | | Oxygen. | | Oxygen. | | Oxygen. |
| Silica | 40.11 | 21.39 | 40.26 | 21.41 | 24.98 | 13.32 |
| Alumina | 35.03 | 16.39 | 34.78 | 16.27 | 20.52 | 9.60 |
| Iron Oxide | 0.81 | 0.24 | 0.63 | 0.19 | 0.59 | 0.18 |
| Lime | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Magnesia | 0.18 | 0.07 | 0.30 | 0.12 | 0.40 | 0.16 |
| Alkalies | 0.19 | 0.03 | 0.03 | 0.00 | 1.41 | 0.24 |
| Water | 12.41 | 11.03 | 12.42 | 11.03 | 7.00 | 6.22 |

If from the quantities of oxygen, as shown in the second columns, we calculate the chemical formula for the clay substance, the sesquioxides (alumina and iron oxides) and the monoxides (magnesia, lime and water) being represented, we get the following equation:

| | Silica. | Alumina. | Water. |
|------------------------|---------|----------|--------|
| Kaolin 1 | 1.92 | 1 | 2.01 |
| Kaolin 2 | 1.95 | 1 | 2.08 |
| Porcelain body 3 | 2.04 | 1 | 2.04 |

The clay substance in all three of these analyzed materials may be considered as identical in chemical composition and corresponds to the formula for clay substance resulting from the disintegration of feldspar as set out by Forschhammer:



There is, however, a difference in clay substances in so far as varying proportions of water have fixed alkalies substituted for them, which, at high temperatures and depending upon their quantities present, must exercise varying influences as fluxes. If we disregard the water, which has no effect upon the behavior of the

clay in burning, and calculate the correlation of the fluxes, alumina and silica, as Bischof did for finding the quotient of refractoriness, we get the following figures:

To one equivalent of flux:

- | | | | | | | | |
|---------------------------|-------|------|---------|-----|--------|------|---------|
| 1. Kaolin from Ledez. | 55.43 | equ. | alumina | and | 106.95 | equ. | silica. |
| 2. Kaolin from Kottiken. | 45.71 | " | " | " | 89.25 | " | " |
| 3. Porcelain body, Berlin | 7.76 | " | " | " | 15.85 | " | " |

However simple may be the relationship and clear the representation of the internal constitution of a kaolin, as shown by the rational analysis combined with the elementary analysis, this, naturally cannot be expected to be the case with clays that are the result of secondary and tertiary depositions; in the first place the primary rock from which the clay is derived cannot, in most cases, be recognized and the simple relationship, as it exists between feldspar and clay substance is not to be found; then, too, the natural slumming process that carried the clay from its original bed, has washed a number of substances into it that have an important influence upon its properties, but which themselves are no longer separately distinguishable from the mass. In the two following tables four clays from the lignitic formation are shown; these can be classed among the purer clays in the lower degrees of the refractory scale. They are suitable for the production of light colored front bricks and for stoneware. The other table exhibits four brick earths, free from lime, which have proved themselves in practice to be peculiarly suited for the manufacture of vitrified bricks (clinkers).

The method of analysis is exactly similar to that described for the kaolins. Instead of the feldspar along with the quartz and the clay substance we shall discover other silicates here, particularly in the brick earths, as these compounds, from their very nature, must be strongly marked silicates, we shall not be far from the truth if we assume that they contain an equal proportion of silica as feldspar does; that is, for each 1% of alumina and iron oxide present in the insoluble residue 3.51% can be taken as silica belonging to the insoluble mineral detritus; the rest of the silica is calculated as quartz.

II.

White, or yellow burning lignitic clay, free from lime.

4. Clay from the Greppin works, near Bitterfeld.
5. Liegnitz clay.
6. Stoneware clay from Kottiken, near Pilsen.
7. Stoneware clay from Ledez.

| Contains: | 4. | | 5. | | 6. | | 7. | |
|-----------------|-------|-------------------------------------|-------|-------------------------------------|--------|-------------------------------------|-------|-------------------------------------|
| | Total | Insoluble in Sul- phuric acid | Total | Insoluble in Sul- phuric acid | Total | Insoluble in Sul- phuric acid | Total | Insoluble in Sul- phuric acid |
| Silica..... | 54.99 | 19.07 | 76.12 | 52.04 | 59.42 | 26.67 | 66.76 | 37.12 |
| Alumina..... | 27.91 | 1.36 | 14.51 | 1.30 | 27.15 | 1.03 | 20.94 | 0.58 |
| Iron Oxide..... | 2.54 | | 1.83 | | 1.77 | | 1.92 | |
| Lime..... | 0.05 | | 0.00 | | 0.00 | | 0.00 | |
| Magnesia..... | 0.83 | | 0.66 | | 0.52 | | 0.81 | |
| Potash..... | 3.67 | 0.15 | 1.83 | 0.14 | 1.50 | 0.09 | 4.64 | 0.27 |
| Water..... | 9.87 | | 4.94 | | 9.85 | | 4.43 | |
| | 99.81 | 20.58 | 99.89 | 53.48 | 100.21 | 27.70 | 99.50 | 37.97 |

If, according to the rule before given, we calculate the quartz, the insoluble mineral detritus and the composition of the actual clay substance, we shall arrive at the following composition of the clay:

| Contains: | 4. Greppin Clay. Per cent. | | 5. Liegnitz Clay. Per cent. | | 6. Kottiken Clay. Per cent. | | 7. Ledez Clay. Per cent. | |
|------------------------------|-------------------------------|-------|--------------------------------|-------|--------------------------------|-------|-----------------------------|-------|
| Quartz..... | 14.30 | | 47.48 | | 23.06 | | 35.08 | |
| Feldspar and other..... | 6.28 | | 6.00 | | 4.73 | | 2.89 | |
| minerals..... | 79.42 | | 46.52 | | 72.21 | | 62.03 | |
| Clay substance..... | 100.00 | | 100.00 | | 100.00 | | 100.00 | |
| The Clay Substance contains: | Ox'gen | | Ox'gen | | Ox'gen | | Ox'gen | |
| Silica..... | 35.92 | 19.16 | 24.08 | 12.84 | 32.75 | 17.45 | 29.64 | 15.81 |
| Alumina..... | 26.55 | 12.42 | 13.20 | 6.18 | 27.12 | 12.71 | 20.94 | 9.80 |
| Iron Oxide..... | 2.54 | 0.76 | 1.83 | 0.55 | 1.77 | 0.53 | 1.92 | 0.58 |
| Lime..... | 0.05 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Magnesia..... | 0.83 | 0.33 | 0.66 | 0.26 | 0.52 | 0.21 | 0.81 | 0.32 |
| Potash..... | 3.52 | 0.60 | 1.69 | 0.29 | 1.41 | 0.26 | 4.47 | 0.76 |
| Water..... | 9.87 | 8.76 | 4.94 | 4.39 | 9.85 | 8.76 | 4.43 | 3.85 |

From this the chemical formula for the clay will be calculated as:

| | Silica. | Alumina. | Water. |
|----------------------|---------|----------|--------|
| 4. Greppin clay..... | 2.17 | 1 | 2.19 |
| 5. Liegnitz "..... | 2.49 | 1 | 1.92 |
| 6. Kottiken "..... | 2.14 | 1 | 2.25 |
| 7. Ledez "..... | 2.28 | 1 | 1.44 |

To enable us to form an opinion respecting the refractoriness of the clay substance, the above analysis gives the following figures:

To one equivalent of flux there is:

4. Greppin clay...4.66 equ. alumina and 10.19 equ. silica.
 5. Liegnitz clay...4.70 " " 12.67 " "
 6. Kottiken clay...8.68 " " 18.64 " "
 7. Ledez clay....3.20 " " 7.32 " "

It will be noticed that these clays, as compared with the kaolins, contain a larger proportion of silica in the actual clay substance, it

amounts to as much as 2.5 equivalents to one equivalent of alumina; also that the fluxes, as expressed in the figures of the total analyses, belong to the clay substance itself and the proportion of undecomposed rock detritus falls very much into the background as compared with the principal constituents, quartz and clay substance; a constitution which differentiates these clays to an important extent, on the one hand from the kaolins, on the other from the actual brick clays, of which a series of analyses follows.

III.

8. Clay from Rathenow (slummed).
9. Vitrifiable clay from Bockhorn.
10. Vitrifiable clay from Schwarzeuhette, Osterode.
11. Vitrifiable clay from Christiania.

The chemical elementary analysis and the solution of these clays in sulphuric acid gave the following:

| Contained: | 8 | | 9 | | 10 | | 11 | |
|-----------------------|--------|-----------------------------|--------|-----------------------------|--------|-----------------------------|--------|-----------------------------|
| | Total | Insoluble in Sulphuric acid | Total | Insoluble in Sulphuric acid | Total | Insoluble in Sulphuric acid | Total | Insoluble in Sulphuric acid |
| Silica | 61.30 | 35.94 | 70.22 | 53.95 | 77.44 | 63.71 | 61.96 | 39.95 |
| Alumina | 18.87 | 2.50 | 13.67 | 2.82 | 9.82 | 3.78 | 17.56 | 6.16 |
| Iron Oxide | 6.66 | | 6.80 | | 5.34 | | 6.17 | |
| Lime | 0.85 | | 0.00 | | 0.00 | | 20.97 | |
| Magnesia | 1.20 | 0.20 | 1.30 | 1.35 | 1.36 | 2.32 | 2.64 | 4.68 |
| Potash and Soda | 3.30 | 1.23 | 3.37 | | 3.87 | | 7.18 | |
| Water | 8.29 | | 5.30 | | 2.48 | | 3.61 | |
| | 100.47 | 39.32 | 100.66 | 58.12 | 100.31 | 70.01 | 100.21 | 50.79 |

*Fe S₂.

If we calculate from this the allied mineralogical constituents:

| Contained: | 8 Per Cent. | | 9 Per Cent. | | 10 Per Cent. | | 11 Per Cent. | |
|---|----------------|-------|----------------|------|-----------------|------|-----------------|-------|
| Quartz | 27.17 | | 44.06 | | 50.64 | | 18.33 | |
| Feldspar and other mineral detritus | 12.70 | | 14.06 | | 19.37 | | 32.64 | |
| Clay Substance | 64.13 | | 41.88 | | 29.99 | | 49.03 | |
| | 100.00 | | 100.00 | | 100.00 | | 100.00 | |
| The Clay Substance Contains: | Ox'gen | | Ox'gen | | Ox'gen | | Ox'gen | |
| Silica | 25.36 | 13.52 | 16.27 | 8.67 | 13.73 | 7.32 | 22.01 | 11.74 |
| Alumina | 16.37 | 7.66 | 11.85 | 5.55 | 6.04 | 2.83 | 11.40 | 5.34 |
| Iron Oxide | 16.66 | 2.00 | 6.80 | 2.04 | 5.34 | 1.60 | 6.17 | 1.85 |
| Lime | 0.85 | 0.24 | 0.00 | 0.00 | 0.00 | 0.54 | ... | ... |
| Magnesia | 1.00 | 0.40 | 1.30 | 0.52 | 1.36 | 0.54 | 2.64 | 1.06 |
| Potash and Soda | 2.07 | 0.35 | 2.02 | 0.34 | 1.55 | 0.26 | 2.50 | 0.43 |
| Water | 8.29 | 7.36 | 5.30 | 4.71 | 2.48 | 2.20 | 3.61 | 3.21 |

The relative equivalence for the clay substance is as follows:

| | Silica. | Alumina (+ iron oxide). | Water (+ alkalis) |
|---------------|---------|-------------------------|-------------------|
| Rathenow clay | 2.09 | 1 | 2.57 |
| Bockhorn " | 1.77 | 1 | 2.19 |
| Osterode " | 2.47 | 1 | 2.08 |
| Christiania " | 2.45 | 1 | 1.65 |

And the relation of the flux to the silica and alumina,

One equivalent of flux:

| | | | | | | |
|---------------|---------|-----------|---------|-----|-----------|---------|
| Rathenow clay |to | 3.22 equ. | alumina | and | 6.83 equ. | silica. |
| Bockhorn " | | 2.94 | " | " | 5.04 | " |
| Osterode " | | 1.85 | " | " | 4.57 | " |
| Christiania " | | 1.61 | " | " | 3.94 | " |

If these determinations, even when not taken very strictly, cannot fulfill all the demands of science they nevertheless give us a very useful, practical insight into the constitution of our clay and provide analyses that are much clearer and more applicable to practical needs than the ordinary general analysis, particularly in respect to the behavior of a clay in high temperatures and this is done without too greatly increasing the labors of the analyst.

We are indebted to the valuable work of Bischof and Riechers for the light that has been thrown upon the behavior of clays in high temperatures and to these investigators the credit is due of having established the significance and the effect of certain substance as fluxes and also as a resistance to melting. The representation in figures of the degree of refractoriness of a clay, which Bischof based upon the analysis, assumed that all the substances, shown by the analysis to exist in the combination, should take part in the reaction at the high temperature. This is by no means always the case, particularly with the silica in the form of grains of quartz and the figures that are calculated, in many cases, do not give a true expression of the actual resistance of the clay to high temperatures. Least of all do these figures agree in the case of, comparatively, easily fusible clays, in which the presupposed chemical reactions are very sluggish or do not take place at all. As a clay mass at a high temperature does not begin to flux in all its parts at the same instant, but only certain portions and these react, chemically, upon the more refractory parts, acting as fluxes upon them, it seems to be of great importance for forming a correct judgment as to the refractoriness of a clay, that we should know something about the greater or less degree of fusibility of the independent as well as the chemically homogeneous constituents and take account of their relative fusibilities as well as their quantities. For this purpose the analytical method indicated above seems to be

altogether better suited than the one that has been; hitherto, in general use, and if the general rules established by Bischof are applied to the similar constituents of a clay the results in the shape of scientific conclusions and practical proof would become very much nearer and, in most cases, would be in complete agreement. I propose, later, when a larger number of analyses of this kind are available, to return to this subject.

The Potteries of Staffordshire.

There are very few industrial districts which claim so great an interest as the pottery cities of Staffordshire, not only on account of the variety and gigantic magnitude of the manufactures carried on there, but also, in much higher degree, on account of the universal and undisputed reputation throughout the world which the products there brought forth have enjoyed for a long time, both in an artistic and technical regard.

The principal manufacturing sites of the Staffordshire potteries have their center at Stoke-upon-Trent, in the broad main and tributary valleys of the Trent, which here form a wide basin; and are concentrated at the cities of Longton, Fenton, Stoke, Etruria, Burslem, and Longport and a number of other smaller places. It is a peculiar sight, which in magnificence can well vie with our most renowned manufacturing places, if one coming from Derby enters this manufacturing circuit at Longton. The peculiarly expanded structure of the English cities with their broad streets, low-built houses, and innumerable chimney-tops, which are planted like organ-pipes on the roof-ridges, lends them a singular character. The numerous cities and villages of this district, wrapped in an everlasting grayish yellow veil of coal-smoke, appear drawn together into one mammoth city, out of which, on the journey through by train the hundreds of forges of the numerous coal-mines and iron-works, the mighty cones of the countless potter's kilns emerge spectrally out of the gray air on one side to vanish back again; and, between these, great rubbish-heaps, deep clay-mines, brickyards, depots for building materials, which are brought from far away for the purposes of the industries, and the products which go hence to all parts of the world, and which consist in coal and iron—but for the most part in ceramic productions of all kinds: stoneware pipes, fireproof bricks, common and black-glazed brick, flags, fine flint-ware, earthenware, parian and soft porcelain.

Of all the industries pursued here, the potteries demand our attention for the most part; and indeed they are what have won for this district its worldwide renown. We shall therefore take a view,

in the first instance, in this direction. One would get a false notion of the too imposing industry if one should suppose that it is only the local conditions that have made the gigantic growth of such an industry inevitable at this very place. Indeed the whole district rests on the vast bed of a rich deposit of coal, which is covered over by productive layers of brickearth and fireclay, in the midst of an extensive canal system and overlaid by railroads leading in all directions like a spiderweb; but the chief materials for the especially characteristic industry of this region today, the materials for the manufacture of fine flintware, so-called earthenware, china and parian porcelain, are not to be found here: they are brought hither from other parts of England and Wales, mainly from Cornwall and Devonshire.

Called forth by the extraordinarily favorable local conditions and the presence of an excellent fireclay, there existed here already ages ago an extensive pottery industry, which, working originally for the supply of a narrow circuit, has risen, through the efforts of men whose names are recorded in the history of nations in letters of gold, and whose example incited their fellow craftsmen to similar efforts, to such significant heights and perfection as we find here and as it alone stands in the pottery industry. It was the Ehler Brothers of Nuremberg who first transplanted their art hither, and before the time of Allen Wedgewood, the great master potter and founder of the greatness of the English clayware industry.

The manifoldness which the manufacture here possesses, which is adapted to the different purposes that clay products have to serve for all the necessities of life, catch the eye here directly; and there is no product, from the imitations of Chinese and Japanese porcelain down to ordinary brick, that does not find here a whole series of representatives which are able to represent it worthily. Should we and could we give here a list of the firms and of their excellently wrought products, we should have to go far beyond the limits of this work. It suffices to say that factories which represent the ceramic industry are to be numbered by hundreds, and the kilns, to be found in the same business, by thousands, without counting the numerous collieries and ironworks. Here even the whole populations of great and wealthy cities are connected either directly or indirectly with this industry.

But it is not only the manysidedness of the manufacture, it is the quantitative side that at first strikes the eye of the visitor overpoweringly, and is able to influence him with a certain reverence for human intellect and human activity. In no small degree is it the quality, the durability of the products wrought which we vainly seek in German potteries, and which we should take as an example:

the accuracy in the purely technical treatment of the material, and the elegance, the taste, and the beauty which the Staffordshire products exhibit in form and decoration, even of the commonest, most ordinary, and cheapest productions, and which have won for them a worldwide renown and a market far beyond the bounds of England. Here we find nothing of the coarse kitchen-pots and awkward pitcher-shapes of our dear fatherland, of the endless rough plastic decorations as they go forth from German factories, and of the clumsy paintings on ordinary vessels. Here everything in these, I might say, commonest products, breathes an elegance, a borrowing from the beautiful, slender forms of the Grecian pottery, which, through the influence of Wedgewood's, is imparted to all pottery, and a manner of painting with the assistance of all technical aids which we are wont to see elsewhere only in the best products. In a word, it is not only the excellence of the material, but a special skill which enabled the Staffordshire potter to bring forth better products; it is not a higher price which a more careful work might command, it is a certain feeling for beauty and an active emulation in the individuals which determine them to furnish something better than proceeds from other workshops. Of course the potter here has also a good school behind him. The influence of Wedgewood may still be felt in the present generation, and will be preserved long hence likewise. Here the industry is conscious of its strength, and the individual feels only too well that naught but an active striving to advance can keep his head above water in the broad stream; that he can then only persevere if he aspires, for his part, to the production of the most excellent products. He is also too practical a business man not to aspire to this advantage out of misapplied regard for economy—that hereditary defect of our German minor industries. He knows, too, that this end cannot be attained without a proper school and without continually learning more, and therefore contrivances are called into being which are intended to make the pottery industry progress steadily on the beaten path.

In Burslem, Stoke, and Etruria have arisen Wedgewood institutions, that is, pottery schools. The fund for the establishment thereof was produced solely through voluntary contribution, without any aid from the state; and through such contributions these schools are sustained, provided with libraries and collections. Therein are taught all the arts and sciences that seem advantageous to pottery-making. These institutes, sprung from the discernment that only practical teaching and practice and the improvement of the taste by producing beautiful models can maintain the exercise of the craft at the heights once reached, breathe forth these ideas to which they owe their origin. They are to be looked upon as the elegant build-

ings of this region, for all the rest are purely practical and devoted only to the technical requirements.

In a review which we give to the Staffordshire industries, those very products which indeed represent in importance the great mass of produce but have otherwise nothing particularly striking about them: namely, the manufacture of firebrick, common brick, terra cotta for building purposes, sewer-pipe, chimney-tops, etc., we can neglect; especially as we are going to return to the discussion of the peculiarities of English brick manufacture, when we have an opportunity; and will confine ourselves, properly speaking, to the nobler products: the vessel-pottery in earthenware, stoneware, and porcelain.

In the examination of the methods of the manufacture of these products, we shall, of course, not be able to enter into the minute details of the great differences of practice in the numerous factories; for the products in one factory, even if they bear the same name, are, neither in the composition of the mass and glaze nor in the style of decoration, strictly like those in the others. We must, therefore, limit ourselves to giving a general idea of the methods of procedure and to indicating how one can reach the same high results in other places, if the matter is taken hold of in the right spirit.

As I have already stated, the materials for the stock productions, fireclay of excellent quality for calcine-brick, pipe, etc., are found in the next district to the industrial region; but not all the various materials which the potter uses here for the preparation of his masses for the finer products, and there is hardly a place on earth that fulfills in this regard all the desirable conditions. However, it is no art to produce something available, yet not just worthy of human creation, when the producer can refer to the rich treasures of nature that fall to him without his help and effort as the main cause of the excellence of his products. The greatness of industrial genius shows itself in that it knows how to produce the conditions necessary for the success of its work; that it understands how to seek in other places where there are natural deposits, and to remove these deposits and make them serviceable for his own purposes; and we find the effect of this industrial genius very distinctly marked here.

In earlier times, the manufacture of pottery was pursued on ground consisting of stores of plastic material heaped up by nature, and vessels were wrought therefrom as good and as bad as we can observe in a hundred other places; and that was the inevitable manner of the development of the industry in question. However, those potters did not adhere permanently to the exclusive conversion of their own clay, but attained, little by little, to giving forth

products of a more beautiful aspect and greater durability, using other materials therefor. They observed that certain other clays, used as additions, imparted to the potsherds a better color; that certain minerals, firestone (a kind of flint), Cornish stone, mixed with the clay in finely distributed condition, gave it a greater hardness and density; that the addition of bone-dust made the burnt clay transparent; and they have gradually come to know what are the proper materials to banish almost completely from their strictly finer manufactures and what to retain only for the repairing of the kilns and saggars and for ordinary products. However one may assert it, therefore, the industry is not of natural growth here; or should one transfer it to where only china clay or Cornish stone or flint is to be found, but where the other materials cannot be had also?

In bulk and entirety the raw materials are the same for all the products made; they differ only in the proportions of their mixtures; and in many cases it would be difficult for a layman to tell an earthenware plate from a stoneware plate, and the latter from a porcelain plate, as he would lack the necessary knowledge of the characteristic marks of these productions. The outward, superficial appearance thereof is always the same; the potsherds are always more or less white, the glaze is always thin, hard, bright, and free from cracks; and the producer is free to furnish the earthen vessel with the same china style of painting, under and over the glaze, as that in the finest porcelain.

In order to apprehend the coarser features of the character of the products of this region, we should first grasp the distinctions as they are made here, and which vary somewhat from German relations. By earthenware is understood such ware as bears always an easily-fusible, transparent glaze, colorless or colored with metallic oxide, on a more or less white, opaque, hard-burnt potsherd; and the term is applied to vessels for all manner of domestic requirements and ornamental purposes and decorated in the same way as porcelain in the matter of printing, painting, and gilding; and possesses, in many cases, the whiteness, hardness, and resistance, but never the ring, of porcelain. This sort of production forms indisputably the bulk of the manufactures. The mass is composed of fire-clay from Devonshire and Derbyshire, together with greater or less additions of china-clay and flint-dust and Cornish stone, a kind of weathered granite from Cornwall, void of mica but rich in feldspar. In this class of products are to be counted the often exceedingly beautiful vessels from the common red brick-clay occurring there, which are partly engobed with white or mottled clay, partly rough and provided with a transparent glaze, or even covered with a very beautiful black enamel, by which a gilding is handsomely set off.

Stoneware is of a thicker, somewhat transparent white or yellowish potsherd with a shelly fracture, mainly wrought into waterjugs, closet-funnels, wainscotings, vestibule-tiles, crocks, etc., perfectly tight and dense, and therefore provided, for the most part, with only an exceedingly thin salt-glaze; but stoneware is also employed for food-dishes and covered with a transparent lead-borax glaze, and mostly printed or dotted with blue or green smalt or chrome colors, or even partly engobed with colored clays.

Parian porcelain, a most highly transparent mass, especially made use of for statues and objects of luxury, has a pale yellow hue and waxy appearance, but, on account of the very great shrinkage it undergoes in burning, it is very difficult to handle and is therefore practicable only for objects of small dimensions. The mass consists of china-clay, Cornish stone, and flint, with a strong addition of burnt bones; is mostly without glaze; but is manifoldly covered with painting, enameling, and gilding. China porcelain, a mass which in whiteness and transparency equals the German porcelain, but is far from possessing the hardness and resistance of the pure, hard feldspathic porcelain, is made of china-clay, flint, Cornish stone, and greater or less additions of bone-dust, and is covered with a lead-borax glaze.

Furthermore, out of certain factories go forth the famous Wedgewood pottery and jasperware, a sort of diaphanous biscuit porcelain, glazed only on the inside in the case of hollow vessels, whose plastic decorations are always taken from Greek models which stand out white and translucent on a ground of faint, very uniform blue, violet, or green: the most beautiful pottery that has ever been produced. Then there are the renowned floor-slugs and wall-tiles of colored and figured, or inlaid masses of stoneware; and finally those imitations of the artistic pottery work of older times and peoples: the Persian, Moorish, Italian, French, and medieval German works in ornamental pieces: vases, wainscotings, and architectural pieces, in the richest variety.

If, to form an idea of the mode of manufacture, we enter one of the numerous factories and follow in detail such manipulations as are customary for the production of earthen wares, should we imagine, in connection with other branches of the industry, another composition, another glaze, and another style of painting, instead of the masses used there, we shall immediately gain a survey at the same time of the manufacture of parian and china porcelain and stoneware; for in essentials the same accuracy, the same care in the execution prevails for all, so that the standards and indispensables for the manufacture of the one can be transferred, without great modifications, to the others. It is just the characteristic of the whole

manufacture, and it differs very essentially and advantageously from our German pottery industry herein: that the material of less noble attributes receives the same care in the treating as does the common material, and that these potters endeavor to produce objects out of the poorer material which will, at least seemingly through outward appearance, approach the best possible. This is the great secret of the superiority of English clayware over the continental productions: not merely the material inherent in the substance, the properties of the clay, but the life that is breathed into this clay by the working thereof.

The factory of Messrs. Pinder, Bourne & Co. in Burslem is the greatest for earthenware, and we shall take something of a view of the same. By way of entrance to the factory, which stands in the middle of the city, we go into a labyrinth of courts, streets, and alleys, whence, without an experienced guide, we might not be able to find our way out. The individual kilns, perhaps a dozen, lie far apart in order to take up the spaces between them for the jigger-rooms, dry-rooms, and glazing-rooms, and all the appurtenances of the manufacture. Only the spaces which are designed for preparing the masses for the combined apparatus of, as it were, little individual factories, and to receive the finished products are united in one larger main building; the others consist of little one-story houses, which, in relation to the plans in German factories, seem slight and irregularly built. However, the mild English climate permits such a wise frugality, and therefore all the Staffordshire potteries seem established after much the same pattern. In the upper story of the main building, which with its wings clutches, as it were, among the confusion of kilns and small houses and combines them in a whole, are to be found the offices, storerooms, and the studios of the painters and gilders, and in the lower story, the workshops for the putting on of printed ornaments and patterns, the mills and slumming-apparatus, presses for the preparation of the masses and making them homogeneous.

The individual ingredients which serve for the preparation of the plastic masses, in this case flint (firestone) and Cornish stone, are ground in a series of pug-mills with water to a fine slum. These ingredients are afterwards mingled with the mixture of Devonshire clay and china-clay dissolved in water to a soft mud.

The mills consist of round, plain wooden vats of about 2.5 m. in diameter, whose bottoms are paved with quartz or flint blocks, and whose seams are filled up with fragments of porcelain. In the middle of the vat stands an upright driving-spindle with four strong wooden arms, which in their revolution, shove before them four quartz blocks weighing about 600 kg. In these mills the flint and

Cornish stone serving as additions to the clay are ground to the finest impalpable slum, and then added, in quantities of fixed proportion, to the clay dissolved in the stirring-vat. The stirring-vat for the solution of the clay is a round wooden tub with an upright shaft which, by a number of horizontal arms, keeps the clay slum in constant motion and thereby prevents the separation of the individual constituents.

The soft clay-slum, of a rather thick creamy consistency, is drawn off after the other, aforesaid substances are intimately embodied in it; and before it reaches a capacious cistern, it has to pass through a number of sieves, which by a system of clockwork are kept in a constant shaking motion in order to ease the passage of the pulp and automatically cast off the coarse parts retained in them. The upper sieves are of brass wire and of the greatest mesh-width for the purpose of holding back stones, roots, etc.; then the sieves become ever finer down to the finest hair-sieve. Such a differentiation of sieves seems necessary for keeping all coarser parts, so far as possible, from the easily clogged, easily torn hair-sieves in order to prevent the collection on them of great masses of sand.

After this operation, the mass appears as a very fine, tangible soft slum of moderately thin fluid consistency, and is raised out of the cistern for the stiffening by means of a suction force-pump, and driven into the filter-press.

The filter-presses, of which there are four, are composed of cells with grooved walls, which are built by the following means. Oak timbers of about 2 m. long and 5 cm. square, and about 20 in number, are so constructed on a frame and secured by bolts and screws that they are held about two or three cm. apart by lists. In each of the cells so made hangs a squeezing-bag of so-called English leather, all which are set in connection with a common tube. Now these squeezing-bags are filled with the fluid clay from the mass-cistern by means of a force-pump. Under the strong pressure of the pump the water is separated from the firm clay; the former flows off through the pores of the squeezing-bag, the latter remains behind; and there is continual driving of the clay-slum by means of the force-pump until the scale of a manometer placed in the tube indicates that further filling is impossible, because the clay in the squeezing-bags has reached such a consistency that it cannot, through pressure, give off any more water.

Now the presses are taken apart, the bags opened, and the mass appears in plates of about 2 m. long, 5 m. wide, and from 2 to 2.5 m. thick, in such a state of stiffness as is suitable for further working on the potter's wheel. Here, however, does not end the preparation of the mass, but the plates of clay are now rolled together

and submitted to a good, effective clay cutter which continues making the mass homogeneous. Finally it passes, formed into handy balls, into the hands of the boys, who immediately cut through it on all sides again on the turntable before the working, and clap it together again in other shapes.

The turning takes place when almost all products made here bear either inside or out, plastic raised ornaments, according to the purposes for which they are intended; as, plates and keys: leaf-and-fruit wreaths on their rims or middle surfaces; jugs and jars: leaf-ornaments, scutcheons, or figural representations on their bellies and necks, etc.—almost always in gypsum molds set on the usual potter's wheel with gypsum top by a boy for that function. Only such objects as must keep a smooth surface within and without, and therefore require a later after-working on the jigger are turned roughly offhand. After the clay-balls are weighed out beforehand, they are laid on the top of the jigger in the designed form, rough-cast on a gypsum plate by means of a gypsum block into a round or oval plate as uniformly thick as possible, after the pattern of the object to be finished therefrom; and, in the revolution of the jigger, impressed, with the hands and a smooth plate of leather or gum, in the outline of the mold. The free plate then preserves its shape by means of an overlaid model of glazed clay, which imparts to the same a perfectly smooth surface.

In the small individual workshops, which are always intended for only one kiln, there are, as a rule, only two or three jiggers in activity. Then beside these shops is a drying-room with scaffolds on its walls, on which are disposed the pieces of work remaining in gypsum molds, and with an iron oven in the middle in which is kept a temperature of from 30° to 40° C., wherewith the gypsum-molds are soon emptied and can be used again. All pieces molded in gypsum remain in the drying-room almost until the completion of the drying, which, in the high temperature of the drying-room, does not demand very much time. Then they come again to the jigger, are set loose in a deepening in the top thereof, where, in a few twirls, the corners and seams derived from the mold are taken from them by means of a fine blade: the last stroke is given to the molding of them.

Such objects only as have smooth surfaces, and are thus given just a rough preliminary turning, are dried more slowly by a mild heat, turned off in the leathery condition on the jigger, and smoothed by means of a steel blade or a glazed piece of clay. Likewise all such objects as require the putting on of handles, spouts, or ornaments, are taken from the gypsum mold in the leathery condition; these parts, which are also pressed out in the gypsum

mold, are glued on by means of clay luting; and then the possible seams and corners are cleaned off.

After drying completely, the vessels come for the first time to the biscuit-burn in the kiln, and here undergo the sharpest fire; whereas in the second, the glaze-burn, because of the fusibility of the glaze, they are heated less strongly, and indeed the burning always takes place in elliptical saggars of equal size: about 50 cm. (19.685 in.) long, 30 cm. (11.811 in.) wide, and from 20 (7.87 in.) to 25 cm. (9.84 in.) deep, with 2-cm. (.7847-in.) wall-thickness. The saggars are built up in pillars under the arch in the kiln, and filled with the green wares without the laying between them of waddings, tripods, or tops, at least for the biscuit-burn.

The kilns used here exclusively for all branches of the pottery-craft and, with a few slight alterations, for the burning of brick and fireproof products, are known as the Staffordshire kilns, and are adopted in all English pottery districts. These kilns are circular with a cupola of about 4 m. (157.48 in.) diam. and 3.5 m. (137.795 in.) height, and provided with from 8 to 10 fire-places on the floor which rises in a gentle slope towards the middle. In the middle of the kiln floor is a circular opening which is connected with the individual fire-places by as many channels. Moreover, each fire-place on the kiln floor has an opening to the burning space around which, to break the melting flame that enters therein, a flue about 1.5 m. (59.4 in.) high is built up loosely of firebricks, with numerous joints, which forms at the same time a kind of pillar. In the middle, over the opening, is erected a similar flue of rings of saggars. For the outlet of the smoke there is, in the middle of the arch, a large opening of about 30 cm. (11.811 in.) and some ten smaller ones in the abutment, which can be shut at need by laying plates on them. The whole is inclosed in a cone-shaped brick mantle, which leaves space on the kiln-floor for going about and narrows to a chimney at the top; this is to protect the kiln and the work therein from the inclemency of the weather. The fastening of the kiln is accomplished by laying around it bands of flat wire-rope.

When the kiln is set with filled saggars and the joints of them are tightened with fireproof clay by the interlaying of thin clay-mud, the entrance-door is walled up, and the firing begun. The burn commences slowly, mounts to the intensest white-heat, and ends after from 36 to 40 hours. The burning-places are mostly without grates, a sort of leanto oven, and can therefore be employed only for very good large-lump coal. At the end of the burn the kiln is emptied again, the vessels taken out of the sag-

gers, dusted off by means of a hair-broom, and taken for the coloring and glazing into the rooms intended therefor.

The colors employed are put on, almost exclusively, under the glaze, and the way in which they are put on is so different from the crude manner customary in our potteries that we must enter more particularly into these manipulations.

The putting of bands and rings on round vessels offers nothing peculiar; it is done with hollow dishes on the jigger and with flat dishes on the jigger-top with the paint-box. But the laying on of fine patterns, leaf-garlands, flowers, and pictures after the printing-process is interesting, and is accomplished by two different methods.

The first consists in the following: The patterns or pictures are engraved on copperplates, stamped on fine silk-paper between two warm rollers, and a varnish is used as a color, in which varnish the colors to give the decorations; cobalt for blue, manganese for brown and black, after they are cut out of the sheet of paper, are laid, piece by piece, with sticky sides upon the biscuit; pressed on tight by rubbing with a felt wad; and thereupon dipped in water. Thereby the paper is loosened and taken off, and the object pressed thereon is left behind in perfect clearness on the biscuit. In this wise the outer contours are imprinted for colored painting, and the further painting is put on by means of the brush with oil-colors. The painting of plastic relief decorations is likewise done with the brush.

By copperplate printing with deepened engraving only fine lines are transferred. Therefore, where larger surfaces of the same color are to be produced, another method of procedure is necessary; namely, that the patterns, with raised forms of wood or stone, are imprinted in a sticky varnish on paper, and this varnish is transferred, in the manner described to the biscuit. Thereupon the sherds are primed; that is, provided with a coating of glue or white of egg, and after this is dry the colors are sprinkled on in the powder form by means of a tuft of cotton and rubbed in. In the subsequent washing with water all the colors are detached again with the glue and come next to the varnish-covered pattern, while they remain clinging to the varnish itself and let the surface stand forth again in all its clearness.

All printed and painted objects must, before they are covered with the glaze, be freed from the oil that has served for the strengthening of the colors, because the glaze-slum to be put on would not stick thereto. This process is as follows: Before the objects are dipped in the glaze, they are set in a large muffle

built of calcine-plates and therein heated to a red glow, whereby the oil is destroyed and burnt up.

One cannot believe, however, that this pretty costly and minute mode of decoration is employed everywhere and under all circumstances. Rather it prevails only for such productions as must certainly offer a compensation for the most costly porcelain, and are therefore bound to come as near to the latter as possible in decoration and painting. For ordinary dishes the method is much simpler, but nevertheless yields most tasteful decorations. Simple uniformly colored arabesques, stars, and dots of recurring patterns consisting of borders, etc., are put on by means of a common sponge with water-colors. On a common bath-sponge with fine pores a larger or smaller flat side is prepared with a sharp knife, and on this surface is cut out the pattern in question; for example, a bough, or an arabesque. Now the sponge is drenched with the color-fluid and this is put on the biscuit by daubing with the sponge.

Furthermore, a decoration of dishes is frequently effected by narrower or broader rings of white pipeclay, or of clay mixed with strong coloring substances, as cobalt-oxide, manganese; especially on those which are prepared with red or yellow-burning fireclay of the clay-pit. These layings on are always done before putting on the handle of the vessel, and therefore in the leathery condition, and on the jigger, during the revolution of which the colors are laid on by means of the paint box. These white or colored stripes projecting from the ground-mass form frequently and oft the ground for the laying on of leaf-wreaths or arabesque features, which are produced by printing by means of dotting or by the brush offhand; so that the greatest variety is observable in this connection.

A most elegant decoration on vessels, which is made without any tools and which the writer had no opportunity to observe in other products, consists in mosslike or treelike branched lines, which, because of its simplicity, can be recommended for products which are less susceptible of a very artistic adornment. It is accomplished in the manner in which one sets the vessel to paint in motion on the jigger, puts on a ring of the same or other coloring clay, and into this slip, so long as it is clean and the water is not yet absorbed therefrom by the ground-mass, lets fall thereon, by means of a sponge or otherwise, a drop of a strong clay coloring fluid, which thereupon immediately blends and forms a treelike design, as one can observe it frequently on the fractured surface of the red clay; which effect cannot be produced in like elegance

and clearness either by printing or by the brush. Should one choose, for this fluid that is to be dropt on, a solution of chrome-alum, then the designs will be green after the burning. A solution of cobaltous chloride colors blue; a solution of manganese vitriol colors from violet to black; and by mixtures one can get every possible tint.

But let us return in our roundabout course to the description of the mode of manufacture. After the decoration by painting or printing, and the burning off of the oil needed therefore, take place, one can proceed to the glazing of the vessels.

The glaze that is employed is distinguished by its extraordinary lustre and its freeness from hairlike fractures. It consists partly of the same substances as the sherd, and this is the cause for its clinging with such extraordinary firmness thereto. The proportions of mixture fluctuate remarkably in the individual factories and for the individual products; moreover, they are everywhere regarded as a secret into which only a few initiated persons may pry. It were idle to give here quite definite proportions when the same must be modified on employing them for another clay. The substances of which the most colorless glaze is composed are flint-dust (silicated), chinaclay, Cornish stone (feldspathic), white lead, and borax, to which substances, as a rule, some smalt is added for the somewhat yellowish coloring of the sherd and for concealing the glaze.

The glazing materials are ground to the finest possible state in the grinding-mills shaken through fine hair-sieves, and the vessels are dipped into the milky fluid. The glaze-slum is always of a very thin fluid consistency, so that only a thin layer ever remains adhering.

After the laying on of the glaze, the dishes go once more into the saggars; which, however, for the second burning are furnished with a glaze inside, so that they cannot touch each other at all and stick together. Therefore, on the bottom of the sagger three-sided strips of clay are laid; between the individual pieces tripods, clamps, and points are inserted so that a melting away is impossible; and the objects are packed in and luted in the same way as in the biscuit-burning.

The burning of the glaze occurs in the same kilns as those here-before described; not only that now the heat is not raised so high because the glaze melts at a lower temperature than is required for the biscuit-burning. In order to ascertain the right moment, a peephole is left above and below in the door, before which stand perforated saggars, out of which by means of a pair

of tongs samples, which lie on small saucers, can be extracted for the judging of the condition.

With this operation the manufacture is properly ended; though often in the case of fancy pieces it happens that afterward a still further decoration by painting with colors over the glaze, gilding, lustring, etc., is imparted. However, this treatment is not peculiar to the products under discussion solely, and we can therefore conveniently pass it by.

If in the foregoing I have undertaken to give a description of the Staffordshire industry, yet no complete picture of the pottery business in this interesting district can be unfolded. The manifoldness of the productions here is so overwhelmingly great that it will have to give us much more material for instruction. There should be brought before the German potters a picture of how it is possible to reach, by restless study and indefatigable zeal, a height of the industry as it exists only in our vocation; and it should be shown that here it is not merely the favor of circumstances which let the brethren of the craft climb to the highest round, as we find elsewhere; that it is not better material, but intelligence and muscle that here celebrate a triumph; and that the same results are to be striven for in other places. The German art industry, and especially the plastic art, has once been that which flourished the most beautifully in the civilized world; may it now again arise from where it has sunk,—not hopelessly indeed,—take example from foreign productions, and once more shine forth as it did before its decline in consequence of political conditions.

English Brick Manufacture.

To understand the peculiarities of the manufacture properly, it seems necessary to consider first the demands which the English architect is accustomed to put on the qualities of artistic building materials; and for this purpose we shall first examine an English dwelling house. The interior arrangements, as essentially dependent on climatic conditions and on habits of life inrooted from of old, we can quite overlook, and consider only the exterior as that part on which generally a study of the materials employed is conceivable.

It must astonish the layman, if he comes over from the Continent, that, contrary to the conditions in our greater Continental cities, the usually very small English residences appear to lack all adornment and, in one and the same street, to be of a uniformity carried for its own sake even to the smallest details. Indeed noth-

ing is more of a bore than the English style of building. However, if you miss beauty in the highest degree, it has one merit; namely, that by virtue of the excellence of its materials it displays a stability such as we shall seek in vain all Germany.

It is characteristic of English residences, and this holds true of all buildings with the exception of that purely monumental class, that the rubblework excels in one way as it does nowhere else: that roughcast on the outer wall-surfaces seems quite unknown in certain regions; and where a roughcast in constructed, it is to be regarded, as a rule, as an ornamental, not as a protective portion of the wall; as, the trimmings of door and window frames, plinths, and mouldings to imitate in most cases, the hewnstone that could otherwise be used here for this purpose. A building whose whole wall-surfaces are covered with a roughcast is extremely rare; more often, to the contrary, in order to hide the discoloration entering through the influences of the weather, especially when yellow bricks are used, a coat of oil-painting is immediately employed on the bricks.

Yet this marked uniformity in the exterior of the building, without sharp projecting structures, without making extremely perceptible the separate stages, without window-arches and cornices standing out either through coloring or materially, without even eaves, if it constitutes the rule in urban and country houses, we do not find everywhere; but in particular cases, especially in public buildings, hospitals, railway stations, etc., we find just the opposite: an overloading partly with raised plastic ornaments, partly with geometrical figures and in mottled, glazed, and unglazed bricks, mosaic tiles, and terra cotta; which, in its restless vivacity of color that runs through all the hues of the rainbow makes the same unpleasant impression for the unaccustomed eye as does the uniformity of the common buildings. A less pretentious decoration than the aforesaid is frequently wrought which is most pleasing; namely, that after a set rule, part of the wall-surface is composed of bricks of various colors. For example, one does not seldom behold buildings that are constructed of yellow bricks; all outward projections, as door and window arches constructed of red bricks; or again, the projections appear black on red ground; but seldom the opposite: the bright brick-colors always have the preponderance in their surface expanses.

If I have said before that English houses are pretentious in their rubbleworks, this holds true not only for the great wall-surfaces, but also, where these are to be found, or project over simple ledges as cornices and window frames, chiefly for the ornamental parts

of the projecting material. Indeed, sandbrick, which undoubtedly forms the fittest material for such purposes as balcony-posts, round wall-pillars, capitals, etc., has obtained the first rank for very widely carried out ornamentation, however; namely, door and window frames, mouldings, friezes, medallions, etc., are as often composed of terra cotta.

After this short description it will be clear to everyone where brick manufacture has to direct its aim; namely, not, as is unfortunately the case in Germany and also in other countries, merely to develop a material that possesses the firmness to bear the weight of the building resting thereon; to form bricks which have an approximately regular shape, where there are no unevennesses and flaws, when these can be hidden by the wide joints and, in a case of necessity, by the plaster, but here there are bricks of the greatest regularity of form and color attainable and the highest degree of durability in weather to be striven for; and how far the English brickmaker strives to reach this goal and really reaches it, a glance at every place of building and every brickyard teaches. It does not seem at all like a patriotic work, always to seek wares in distant places, and to hold what is produced abroad to be better and praiseworthy under all circumstances; but it is not well to content oneself in narrow selfcomplacency with one's own products and put them topmost. But if we must admit that, especially in latter years, partly through the efforts of the brickmakers' association, in Germany, a lively competition has sprung up in our territory, yet we cannot blind ourselves to the observation that this competition, particularly in the district of its sister industry in England of producing materials for roughcasting, seems yet far from matured, if it is considered in regard to its comparative advantages in fuels; that there is much left for its to do; that it must lay aside many of its defects in brick manufacture before it can reach the highest round.

Still we shall not judge onesidedly and lay all the blame on the brickmakers of the decline of their industry. There are other causes, to say nothing of the political conditions and the lack of selfconsciousness called out thereby, which things have hampered them in many directions; part of the blame, however, falls in any case on the architects. Had our master builders recognized earlier what invaluable materials they possessed in a well-made weather-proof brick, both as common building brick, ornamental brick, and terra cotta; had they likewise earlier set higher requirements as they begin to do often today on the utility and advantage of both parts, then would the brick manufacture have taken an ascent

earlier along with the general importation of roughcast; and also the ornamentation of buildings in Germany would have taken a less tasteless direction than we see in English architecture.

Equally certain is it that English brick, in large proportion (for where there is light there is also shadow, and along with good wroducts, one sees bad ones here, too), must become more renowned than the German brick, on account of the more careful preparation which is given to the clay, whereby the products wrought therefrom obtain also the qualities corresponding to their destiny and mode of application. The English brick is always distinguished by a great homogeneity and above all by a great regularity of form, even the common back-wall and foundation bricks; and are handled with a carefulness and delicacy to keep the edges and corners in safe condition, that people here in Germany could take example from. The latter characteristic extends even to the mason; and it is always of the greatest importance for the roughcast to build with much tighter joints, as if to lay the bricks with only a limited quantity of mortar for cementing.

In order to form an idea of how an artistic style of architecture is attained in England, it is necessary to examine the mode of working in various places and with various materials; and we shall begin here with the commonest kind of manufacture; with the traveling kind, we might call it, which sets up its place of operations in the neighborhood of the building for which it works. This method we find working in the charcoal-kilns in all the suburbs of London.

For the raw material, the clay, one has not far to seek there; for London lies in a basin which is filled with a very great deposit of a very beautiful, uniform, and extraordinarily pure and plastic clay. Sand is also in the neighborhood as a rule, and so here is established a brick factory, or, more properly speaking, a brickyard, usually on leased ground in the neighborhood of the building for which it has to supply the material. Thus, apparently without any preparations, without foundations, without drying-sheds and kilns, the reader will ask how it is possible to supply bricks that are to serve for roughcast, and indeed not for country dwellings, but for buildings in the English capital. Yes, it is possible, and if the manufacture is not a dazzler to the senses, as we use the designation, nevertheless it is a brick which can compete in the matter of shape with any brick laid on boards; for, to betray the secret at once, it is touched no more from the moment it leaves the mold till it can be put into the kiln.

Late in autumn and in winter, the needful clay and sand are dug

and later sifted in such quantity as is requisite for the building in prospect for the next year; and both (instead of the last pitcoal ashes, which are also thoroughly sifted) are carted into layers varying from about 15 cm. (5.9 in.) thick, to rectangular, regularly formed heaps, while this work is sprinkled with a squirt as evenly as possible; then, for a few weeks or months, according as preparatory work is begun earlier or later the piles are committed to the influence of the weather. As soon as the ice has vanished from the clay-mound in the spring, the process of repeated mixing and settling continues, and thereby the pile is completely worked over and dug off perpendicularly, and the clay that is dug off is thrown up into a similar pile again. During this digging off, water is sprinkled on with a squirt again as it proves necessary, and for the action of this water a few weeks are given again, until the temperature has become so warm that one can begin the work of spreading without danger. Meanwhile all the needful preparations for the manufacturing proper are made; the clay-mills and machines are set up, the drying yards levelled and heightened, so that the work can begin at once.

In England, and especially in London, wages are very high, and therefore machinery is as much employed as is possible anywhere; and so even here, in this most simple mode of brick manufacture, we find it represented to a considerable extent. Before each of the rows of clay-piles heaped up during the winter, or for every two of them, is placed in an equally exact row a number of clay-mills, according to the magnitude of the quantity of brick to be produced; these clay-mills are to work the clay, with the sand and coal-ashes mixed in it, to a homogeneous mass, after the water, by the action of several weeks, has done what is should to the clay to soften it. In certain cases one sees horse-powers in use for this work; in most cases, however, it is performed by steam-power. In a convenient spot, one sees set up for this purpose a locomobile. From this a rope or wire line, passed through pulleys, runs over all the clay-mills that stand in a row at certain distances, winds itself around the drum which forms the organ of its motion, and runs back again over the great belt-pulley of the locomobile. By the motion which is given to the line all the clay-mills on the often very extensive field of the plant are set in motion at the same time in the simplest manner.

As soon as the clay is here formed into a homogeneous and moldable condition, the brickmaking begins. For this purpose the mold-tables are placed, as a rule, immediately beside the pug-mill. It deserves to be brought out here that the English brick molder does not work with stiff clay only, as is customary in

Germany, so that the offborne bricks are set at once on edge, and the work of setting them on edge and the finger-impressions and other injuries thereby imparted are wholly avoided. But he uses also a few artifices which do away completely with a touching with the hands after the molding, and thereby preserve the brick in its original shape. He makes use, expressly for the offbearing, of two little boards of hard, smooth wood as wide as a brick, 2-5 in. thick and 14 in. long. One of these little boards serves in the mold as a base under the frame. When the brick is molded thereon in the usual manner with sand or water, the offbearer lays the second board on top of that, and thereby presses down the corners that stand out on the taking off of the mold, carries the brick to the drying place, and there lets it glide out on its side, as he takes the small boards a little way apart in such a way that between the fresh brick and the one previously laid there remains an intervening space as wide as the thickness of the board. When he has taken off a row of bricks in this manner, he turns to another part of the drying place, until after a day or two the bricks are so dry that they can stand it to have another course laid on them without impression; and in the same way row on row continues to be laid as high as possible. One sees that here occurs a stacking of bricks on their edges, a putting together in courses, etc., all at once; that therein is an economy which is not to be rated high enough, and yet which produces a brick which, in the matter of regularity of form, leaves nothing more to be desired. These rows of bricks are protected from rain, and when necessary, from the effects of the sun, either by a simple covering of straw or by narrow roofs set on posts and covered with straw or shingles, or by portable shingle or reed-thatched roofs laid over them. If the drying places are very extensive, which thing is necessary in the case of the machine-molding to be described hereafter, the bricks are not, of course, carried away singly, but are laid 24 at a time on a wheelbarrow, whose wheel goes in springs in order to prevent a change in the shape of the bricks during the transportation; carried on this wheelbarrow to the place of deposit, taken off between two boards, as already described, and set down.

Hand-molding, at least in the immediate neighborhood of London, is practiced to a limited extent, and as England is generally called pre-eminently the land of machine-work, so even in these temporary brickyards, brick machines have won the upper hand. Moreover, this is a machine which must be specially mentioned here, because the manner and method of its operation seems derived wholly from the hand-molding, and with little assistance, it is

able to turn out a very great number of beautifully squared bricks, if the clay is properly prepared for it.

The machine consists of an upright hopper whose function is not to mix the clay, but only to drive a uniform column of moldable clay out of the broad mouthpiece. Under the mouthpiece is a table driven in an alternating to and fro motion by an eccentric, which is on the axle that passes through the bottom of the mixing tube. On this table are laid the wooden sand-strewn mold-boxes containing the molds for six bricks. These molds are shoved under the column of clay by the forward motion of the table, so that the column covers the molds. Then an iron plate, which maintains an up and down motion on a hinge, presses upon the clay column, fills the six compartments of the mold-box, and when this is done, a new empty mold-box is shoved under, pushing the filled one out before it, and, at the same time that it presses the filled mold-box through a slit of the height of the mold, it cuts off the greater part of the overshooting clay, so that nothing further is necessary but to smooth the brick with a strike and lay it off immediately upon the car that stands ready, and on the little board lying thereon. In order to make possible the most complete pressing in and filling out of the clay in the molds, the bottoms of the molds are not perfectly tight, but have on their long sides thin openings, which allow the exit of the air below and therewith the pressing in of the clay from above.

With one horse for motive power, a man to take off, one to sand the mold and shove under the mold-boxes, two loaders, and three haulers, seven men in all, such a machine can make, with soft plastic clay, from 12,000 to 16,000 beautifully molded bricks a day. The machine is transportable, and is so placed in a deepening of the earth on an arrangement of timbers that a circuit for the horse is possible. One also sees this machine operated by steam power frequently.

The burning of the bricks produced in this way takes place, as a rule, in a pile in the middle of the drying place, with coal scattered, as soon as a sufficient number of air-dried bricks accumulate, and it offers nothing specially new. We can pass over this point all the sooner as we have already, in an earlier letter, on the occasion of discussing Belgian brick manufacture, exhibited this procedure as it is known on the Continent, and shown, on its darker side, this mode of burning brick.

The method thus described is that which is employed for producing the commonest kind of bricks, which bricks are indeed burned very hard, and, when the clay has been carefully worked, suffer less harm by burning the pile than we have seen in the case of the cor-

responding manufacture in Belgium and on the Lower Rhine. There these bricks appear perfectly squared and even, but naturally do not possess the uniformity of color to satisfy the higher requirements. Let the kind reader, therefore, follow me to another brick manufactory whose products, if its bricks are not more durable, yet have a more pleasing appearance; namely, to the manufactory of the Burham Brick Co., of Snodland, Kent.

This brick factory, lying in the neighborhood of the mouth of the Medway, enjoys, on account of the excellence of the brick and terra cotta there produced, especially in London, where a yellow brick is much in favor, a good reputation; and it takes its clay from the same formation whence the common out-of-door brick works of London obtain their material; the so-called gault clay or London clay. The production of this establishment runs from 15,000,000 to 20,000,000 a year, of not only facing and roughcast bricks, but also of terra cotta, building ornaments, and great quadrilateral and hexagonal pipes which, with a concrete composed of cement and finely pounded granite, serve likewise as building material. This factory uses, by the way, the vast deposits of chalk underlying the clay in conjunction with the clay in the manufacture of cement. In the clay mines lying in the immediate neighborhood of the brick works, in which mines the walls of clay stand between 33 and 39 ft. high, the clay is dug in winter and treated in the same way as hereinbefore described; that is, it is put in layers, alternating with layers of sifted sand, hauled to a heap on the bottom of the pit, drenched with water, and spread out for as long a time as possible in the manner of the softening or mixing with water. Out of the clay pit a car track runs on an inclined plane up to the machine building, by means of which track the material for feeding the brick press, after it has been mixed in the clay-pit and, if necessary, resprinkled with water, is passed up on a chain which winds itself over a drum above.

The extensive machine building, which is erected between the driers, contains, besides a 250-h. p. steam engine, four simple rollers for rolling the clay, and 10 Clayton brick presses, each capable of producing about 12,000,000 to 15,000,000 bricks a year, and each provided with a huge pug-mill for preparing the paste. The Clayton press, which has had a wide dissemination in brick manufacture, is built on the same principle on which the Sachsenberg machine, frequently met with in Germany, works. Namely, the clay is moved in a uniform column out of the pug-mill and over a turntable to the press, where it is seized by a pair of rollers lying obliquely one above the other and pressed on into the mold. From

this it passes through a mouthpiece of brass, which, to prevent the leaving behind and tearing up of the clay on the corners, is conical and whose polished surfaces are properly slanted. After the clay has passed two more wet rollers, constructed laterally from the mouthpiece, onto the revolving table; on which table a piece of the column is cut off close to the mouthpiece by a wire, which piece suffices for 12 full bricks and two small sections at both the ends, which sections must be borne in mind. This piece is shoved onto the cutting-table. As is also true here, in distinction from our German machines in the case of rollers and pug-mills, that they seem independent machines, the cut-off apparatus offers a peculiarity in that it does not cut off the bricks directly from the issuing clay-column, but that a piece is shoved to it over a roller running in an oil-holder, which roller smears the under surface of the column; and the piece is so cut through that it becomes unnecessary to take hold of the bricks to put them on the car. The clay is not strictly cut through by a motion of the wires, but by means of a movable piece, which is set in motion by a system of levers, and pressed against the fast-standing wires. After the clay has passed these wires, it is extended on a pallet which is put on a car with the 12 bricks standing thereon, and is replaced by a new board laid before the wires. From the machines the bricks are put on cars, whose wheels go in springs, and then taken to the driers that are built on both sides of the machine building. On the cars the bricks are set on a broken layer of bricks, and they are taken from the cars by means of a two-tined fork, thus avoiding again the touching of them with the hands. The dry-sheds, between which a car space of about 51 in. in width is left, and provided with narrow, two-slope roofs which, at a height of nearly 5 ft. 3 in. above the ground, rests on posts and are covered with shingles. These insure the goods a good enough shelter from the effects of the weather, and little by little, in proportion as the lower tiers of bricks become dry and capable of bearing weight, the bricks are stacked in the sheds full to the top.

On the upper floors and in the wings of the machine house are found the machines for the production of terra cotta, and of pipes which, filled with concrete, serve for building purposes, and the represses for fancy bricks, etc. The greater building ornaments are pressed out as usual in plaster of paris molds. There is only one kind of building bricks which demands our special interest, because they have not heretofore been produced in this variety and perfection in other works. These are ornamental bricks which bear on one, or even on two, surfaces raised ornaments, partly of leaf-wreaths or tendrils, partly of geometrical arrangements of recurring

figures, ellipses, palmettes, etc.; which are so arranged that when the binders and stretchers are put together they form a combined ornament. The number of patterns found here, which serve for the ornamentation of cornices, door and window casings, and arches and medallions, such as are seen in Londoners' residences; and also for the wainscoting of whole wall surfaces, is extraordinarily rich. According to the statements which were made to the writer on the spot, the manufacture last year amounted to 600,000 in 142 patterns, and the work expended thereon was exorbitantly rewarded. The manufacture of these bricks is indeed so simple that the cost of production could not amount to much more than that of repressed bricks. The press used in the manufacture is one patented in England by Mr. Henry Pethers. This press bears the mold, which consists of a bed-plate and four side plates fastened thereto with hinges, on a strong horizontal axle. The press-plate is over this mold and can be driven down by means of a screw and flywheel. Now the mechanism is so arranged that whenever a brick, coming fresh from the machine, is placed on the bed-plate and the die is driven down, the four side-plates are clapped up at the same time by a cam and roller, so that a pressure can be given to the brick on all sides at the same time. The iron models for stamping on the ornaments are fastened on the press-plate or on the side-flaps by means of screws and can be easily exchanged; and one can easily see that here one can at pleasure stamp the ornaments of the brick on five sides, since after the automatic retreat of the stamp, the four side-plates fall back again also, and the finished pressed brick stands free on the bed-plate. Every machine always has on its axle two such folding molds, one for pressing binders and one for stretchers, so that only the axle needs to be turned around, and another press-model screwed on whenever one wishes to produce a new ornament.

According to the statements of the factory, where three such presses are operated, each press turns out 1,000 bricks a day.

The burning of all the products turned out is done in the so-called Scotch kiln, which is the one most used in England, and is closely akin to our common open kilns in structure and operation. These Scotch kilns consist of a quadrangular burning space 10 ft. high, 13 ft. wide, and from 33 to 39 ft. long, built over the ground and having on each of the narrow sides an entrance door for filling and emptying. On each of the long sides are small fireholes 3 ft. 3 in. apart, and measuring about 2 ft. in height, and 6 in. in width, which are divided into two parts in the middle by a brick thrust through, and are so constructed that two always lie opposite each other; the plan, therefore, constitutes a passage for stoking. The

fireboxes are without grates and are fed only with lump-coal in such a way that the upper half of the firehole is always filled with fresh coal, while the lower half always takes in coke made therefrom, which fuels from time to time are poked on into the stoking passage as fast as they can burn there.

The regulation of the fire, which in the case of great expanse of hearth surface, is naturally very difficult, and demands the closest attention, especially in stormy weather, is effected in this way. The fully set kiln is covered over with useless bricks and this covering is made more or less impenetrable by a sprinkling of ashes, and thereby, always according to need, if the circulation of air is entirely hemmed in, or, on the other hand, by the removal of this covering in such spots as seem necessary, a stronger fire-draft is effected.

There are such kilns that hold from 100,000 to 130,000 bricks, placed about 30 in two rows, and therein all the products undergo the burning process.

One will see from the description how the brick manufacture is practiced in the southern counties of England, and that it does not differ, in essential points, from the method of procedure customary with us, and that the superiority of that method over ours is to be sought especially in the greater care with which a uniformity of mass and the highest attainable regularity of shape are striven for, and depends, in economical relations, on the employment of machines and the division of labor which extends to the smallest details. The English brickmaker is not a brickmaker for every department, as is too often the case among us. He is not a clay digger, treader, molder, and burner all in one, but is always only one of these.

In the northern, the manufacture of bricks is developed in an entirely different direction. As the architects there demand as much of it as they do in the south, the quality of the raw brick materials render it necessary to deviate from the otherwise usual method of brickmaking, and to institute a method of manufacturing totally different from all other methods. The brick industry to be discussed now has its seat chiefly in the shires of York, Lincoln, Lancaster, Chester, and Nottingham, and the brick factories are usually in or near the coal-fields of this region. Here a clay, or rather clay-slate, very refractory to water serves as raw material for brickmaking. This accompanies the coal-beds and needs a year of weathering before it can be altered to such a plastic mass as the ordinary sort of handworking or machine-working demands. The difficulties given rise to by the quality of the material have been so controlled that the process for which nature uses a series of

years, is reduced by machine-power to the shortest possible time; and it will seem incredible to the reader when I impart to him that the material which is now taken from the pit is set in the annular kiln as green brick in half an hour or an hour. The clay is not subjected to a softening process, but is finely powdered in the condition in which it is taken from the ground, and in a powerful press is composed into bricks, tiles, mold bricks, etc.

For a number of years this same method has been tried in Germany, but has not been able to make a place for itself. There it produced only a brick material which could in no wise fulfill the same requirements. But if one sees the difference between the efforts which failed in Germany and the practice, as it could make its way on a large scale in England, the causes of the failure today would become apparent, on the one hand, first, the everlasting recommendation of the machine manufacture in question to press good, ringing bricks out of unprepared clay taken fresh from the ground, with so and so many thousand capacity with feeble service; and, secondly, the credulous ones who gave credence to it—on the other hand, colossal steam-power machines in which the main portion of the power is devoted to the preparation of the clay.

Now one will reply to me that the quality of the material generally demands a great consumption of power to preserve therefrom an available means for brickmaking, for it is clear from the foregoing that one can get no bricks by pressing slatestones together and subsequently burning them. However, the dry-press method has become established for not only non-plastic or slightly plastic raw materials, but has made its way also for plastic materials; and one can see that in many places, for economical reasons, the bricks commonly serving for facing are made by the dry-press process, and the ornamental and mold bricks, terra cotta, and floor tiles are produced out of the same unwintered material (for in England, on account of the much milder climate than is the state of things in Germany, the wintering process has a subordinate significance) in the soft-mud condition.

The clay, as nature has laid it in the ground, has always a stratified or laminated structure, and the whole operation of wintering, water-mixing in the pit, hauling, and working in wheel-tracks and pug-mills, has only the object of destroying this structure, to give it that uniformity without which clay products are generally not to be produced without being ruined during the manufacture by crazing and irregular shrinkage, or later, by weathering and disintegration. In the Northern English manufacture, one seeks to destroy this structure inherent in the clay by reducing the same to powder,

and the finer the powder to which one can convert the clay, the better one can reach the end in view.

From all other brickyards English brick works are distinguished by their doing without any dry preparation, and they, therefore, require much narrower ground than we are accustomed to see in our country. They consist of an annular kiln, or an adequate number of Scotch kilns, a machine building, and the clay-pit, which, as a rule, is connected with the machine by a car-track. Before I begin the description of some of the machines in use, I will explain briefly the course of the individual processes. After the raw material is loosened in the pit, it is loaded on cars which, if the ground is horizontal, are run on a railway, or, in case of a lower situation, are wound up by a machine on an inclined plane. The transportation of the clay always ends in one or two mills, vertical edge-roller crushing mills, in which the upper stones do not revolve, as is usual with us, but remain fixed on their shafts, whose journals rise or sink in guides; and the bed-stone, consisting of a cast-iron plate, is set in rotation. The bed-stone, about $6\frac{1}{2}$ ft. to 8 ft. in diameter, has a raised rim, and in its outer portion is pierced sieve-fashion with little holes, so that all the finely ground parts are straightway removed out of reach of the stones and fall into a tin box that is under the mill. From this receptacle the clay powder is hoisted by an elevator to a higher floor, and there passed into a sieve in order to remove all the coarser parts. The sieve has such mesh-width that all the finer parts down to the size of a pinhead go through it and reach the brick-press, while the coarser grains go back for further crushing under the mill-stones or in the disintegrator, where they are finally mashed to a fine powder. The powder obtained then goes through a hopper into the very powerful presses, of which there are a great many different constructions, and are therein made into bricks of such sharpness of edge as could not be otherwise obtained, and also of such smoothness of surface and density that they can be immediately packed close together on cars, like air-dried bricks, hauled away, and set in the kiln. The green pressed bricks have such firmness that they can, without danger be set immediately up to the height of the kiln-arch. Perhaps, indeed, they have a greater firmness than the completely dried common bricks, so that it is absolutely unnecessary to handle them with extreme care. The first operation to which the bricks must be subjected now in the kiln is that of the drying and water-smoking, in which they immediately, as very often happens in the case of air-dried bricks, in an annular kiln treatment, are either consumed in smoking or show so strong a white flux from the great amount of

dampness which they bring with them from the pit, that they can find no employment as roughcast bricks, and that is always the point in England. Where Scotch kilns are employed, this drying and watersmoking takes place in the usual manner with a slow fire, with the difference that here a longer time must be taken therefor, as is the case with dry setting. When annular kilns are used, the water-smokin is done in a totally different way. One or two compartments are always shut off, each by itself, from the part of the kiln in use, so that three slides are needful for this purpose; and in the entrance-hole, which, to give the air full access to the kiln, has a very wide opening, a water-smoking fire is kindled on a temporary grate. The hot air enters the freshly-set compartments of the kiln and the dampness expelled therefrom escapes at first out of the stokeholes above, and later, after the latter are closed and the cover of the compartment in question has been withdrawn, out of the chimney. Another way to expel the dampness and thereby avoid fluxes is to close the entrance-holes immediately after the chambers are fully set, and to put a little water-smoking kiln on each of the fireholes, so that warm air can enter all parts of the dome of the kiln; then the expelled dampness escapes from the beginning through the opened cover to the chimney. The water-smoking kilns consist of cast-iron cylinders of about 16 in. in height and 8 in. in diameter, which have a grate in their under side and are set in the sand-groove of the firehole. Now on the grate is made a fire of poor fuel, ashes from the boiler furnace fire or small coal, and the air, drawn through the chimney and through all the fireholes into the chambers of the kiln, can reach the compartments in no other way than by passing through these small fires and being warmed in them. A third kind of water-smoking is by means of a single water-smoking kiln standing on the crown and transportable on wheels. This water-smoking kiln consists of a sheet iron cylinder whose inside is lined with fireclay, so that there is a firedraft about 10 to 12 in. wide and 39.37 in. deep, which is closed at the bottom by a grate of iron bars. The upper opening serves as a place to pour in the fuel, and is to be covered with an iron slide. Close under the upper opening are fixed four lateral tubes for the outlet of the hot air. These tubes are connected with four fireholes by means of elbow tubes, and the heated air is drawn by the draft of the chimney into the kiln space.

The method of watersmoking to mention as fourth is that which is introduced into all modern continuous kilns, wherein it has been extraordinarily well tested. This is the method of watersmoking

by means of a watersmoking channel, or flue, made between the smoke-gathering space and the line of kiln-compartments. By this arrangement the hot air used for drying is drawn from the compartments that are cooling off, so that a special firing is unnecessary. In whatever manner watersmoking may be done, it must always be continued until the setting is so thoroughly dried and heated that no subsequent condensation on the surfaces of the bricks from the hot air can take place; otherwise the purpose of obtaining pure-colored bricks for brickwork is missed completely. After the completion of the watersmoking between the slides, or partitions, which as a rule requires about 48 hours, the watersmoked compartment is brought within reach of the fire by the removal of a partition, and the watersmoking of another compartment is begun.

The bricks burnt in this way possess a sufficient durability only when they are burnt as hard as clinker bricks. When they are not burnt hard they are more liable to disintegration than are bricks made of plastic clay; therefore one is always intent on burning very carefully. This hard burn is, however, very much facilitated by the manufacture itself, as the mass of clay assumes, under the tremendous pressure to which it is subjected, a greater density than is the case with our machine-made bricks. Consequently the bricks shrink less and are, moreover, not liable to crumble and bend in a strong fire. At the same time, the bricks are finely trimmed on all sides and possess such a regularity of form as one desires in building brick, and such a resistance to shocks as is found elsewhere only in the finest firebrick, which fact is owing to their manufacture wholly out of a granular clay-dust. The resistance to injury from shocks is so remarkable that it is not customary to pack the bricks with precision in the two-wheeled carts for land transportation; but they are just thrown into the cart-box without order, and on arrival at the building place they are simply dumped off.

It now remains only to discuss the presses which are used to combine the loose, damp clay-dust into a dense, compact mass. Among the number of varied systems I shall here bring up two which are mostly adopted and which seem to serve their purpose best.

Driven by a force of about 20 or 25 h. p., the machine of Bradley & Craven, of Wakefield, Yorkshire, together with all the auxiliary machines, including a clay-hoist, two edge-runner grinding mills, an elevator, and a system of screens, can turn out 15,000 bricks a day. This machine consists of a thick iron disk fastened horizontally on an upright revolving shaft. In this disk are cut 12 openings, each of the size of a brick to be repressed: 9 in. long,

4½ in. wide and 3 in. thick. By a large wheel with three cams, this disk maintains a regular jolting rotation. The openings of the disk are closed below by plates which move up and down in guides, and thereby keep up the upward motion needed for raising the brick. In short, during the revolution, the plates glide by means of rollers on an undulatory track. Two wooden tubes, through which the clay-dust falls down, open upon the disk from above, and stand opposite each other. In two other opposite positions two plungers are kept rising and sinking by a powerful eccentric. Let us consider the action of the machine. Whenever an empty mold-opening, or die, comes under the clay-spout, the bed-plate closes up the lower part of the opening. Then the mold, or die, fills up with the loose clay-dust and is carried, in the rotation, away from the mouth of the clay-spout. At the subsequent pause of the disk, down come both plungers on the filled dies, press slowly but very powerfully the clay therein by means of an eccentric, and then rise up again. In the further rotation the bed-plate shoves the brick up and out, and on the arrival of the empty die under the second clay-chute, the bed-plate has returned to its former position at the bottom of the die, so that the die can fill up with clay again. Both the mold-disk and the plungers are cast hollow and are kept always hot by the steam that is driven into them. Thereby is prevented the adhesion of the clay to the molds and the bricks always come out with clean, polished surfaces. Therefore no lubrication is necessary.

Although the second machine requires more force to run it (30 to 35 h. p. with the auxiliary machines), it seems to have come into wider use than the one just described; at least I had opportunity more often of seeing it in operation. This is the press of Platt Brothers, in Oldham, Lancashire. Its wider use may be owing to the fact that the whole mechanism is simplified by the omission of the revolving mold-disk, and that the bricks in this machine are not pressed from above only, but have a like pressure applied simultaneously from below; hence the clay is compressed uniformly. As in all these machines, the clay is taken fresh from the pit, crushed in the grinding-mill, and screened, and the resulting particles are subsequently reduced. On a very solid metallic table, four dies are cut side by side; into these four plungers press down from above simultaneously, which plungers are kept moving up and down by an eccentric. The dies are closed below by four more plungers, which are likewise moved by an eccentric, and which serve not only for raising the pressed brick out of the die but also, driven upward by a peculiar sort of eccentric, at the same time that the upper plungers are driven down, make it possible

to press the clay-dust on both sides. As the upper plungers return to their highest position, the lower ones push the brick up and out. At the same time, a charger, filled with clay under the hopper, is shoved forward, thrusting the finished brick before it out upon an endless belt. As soon as the charger covers the die, the lower plunger suddenly falls down; the die fills with clay, and the charger smooths the top of the clay in its retreat. Then down come the upper plungers again and the foregoing process begins once more. These dies and plungers are also steam-heated to prevent the adhesion of the clay.

To estimate correctly the advantages and disadvantages of the process described, to answer the relevant question in regard to cost, and to decide the possibility of introducing the process elsewhere, it is necessary for us to present to ourselves the circumstances out of which this industry has grown. One must bear in mind that raw material of this region does not generally possess the plasticity which we must have elsewhere for the production of good bricks; that here, therefore, other means than a powerful pressure for the molds must be taken to assist. It is now clear that so close a combination of the clay particles as occurs in the usual process of tempering cannot be effected by the addition of the strongest pressure. It will also be clear that this lack in the manufacture must be made up for by a very hard burn, or the bricks produced will undergo a rapid disintegration. On the other hand, if the conditions for a hard burn are fulfilled, this process has undeniably great advantages. It is very difficult, indeed to obtain, by any other method, such perfect, uniform molding as is done by this process. Finally, these bricks possess a tenacity and a resistance to pressure and shocks that are attributed only to the best kind of bricks.

The Bock Drier.

[The reader will readily notice that the following essay on the Bock drier was written before the artificial driers so esteemed at the present time had come into general use. Hence the conservative tone of the discourse.—Translator.]

The aim of our artificial drying apparatus is to enable brick manufacture, and all those industries generally that claim extensive drying apparatus, to dispense with the slow method of drying in the open air by the help of a gratuitous expenditure of warmth by the sun; and to replace this method with an artificial but powerful source of heat, and thereby to render these industries independent of the difficulties which variation of temperature or moisture in the air, or unfavorable climatic conditions give rise to.

Let us suppose there existed an apparatus capable of removing the water to be evaporated by the drying with the theoretically smallest requisite amount of fuel; then the question remains: Can an artificial and rapid drying be so carried on under these favorable conditions that it will adapt itself to the peculiarities of the material and to the requisites of the whole manufacture?

This question, so far as it deals with clay, cannot be answered unconditionally in the affirmative.

In an earlier essay which treated of drying in the open air and in inclosed spaces, I have developed in a purely theoretical manner the requisites which must be fulfilled in artificial drying apparatus if they are to effect the drying with such a consumption of fuel that they can compete successfully with the common gratuitous but irregular solar source of heat. Hitherto the brick industry has no such drying apparatus. I have herein pointed out that the most favorable conditions for artificial drying when the drying is effected as rapidly as possible are in the highest possible temperature and in the swiftest change of air. These requisites, however, conflict so strongly with the properties of most of the raw materials used in the clay industries that one cannot regard the most striking idea in connection with this drier as the only one to take into consideration.

If an artificial system of drying must therefore be rapid (and all the constructions that have appeared so far have their sole merit in drying swiftly, and can be considered only just as profitable as drying in the open air) it conflicts utterly with the nature of the clay. The brickmaker knows too well from experience that too rapid drying by solar heat and strong wind can do him immeasurably more damage than frost, against which a well-wrought artificial drying apparatus will always afford a secure protection.

It seems to me, therefore, unwarranted to think of simplifying the manufacture of brick by doing in a day or two by artificial means the drying which, under favorable conditions, demands 14 days in the open air, and usually much longer; and which drying cannot, according to experience, be considerably shortened without harm, at least with most clays. Here and there, there are indeed materials which will stand such treatment; but this is only in rare cases, and, as a rule, the impossibility of such a shortening of time will become apparent all too soon.

As to the form of the Bock drier, it corresponds outwardly to that of the tunnel-kiln. From the latter are borrowed a whole series of details, although the inner structure is essentially altered to suit the different purposes of the apparatus. The drier consists

of a long, straight tunnel with rectangular cross-section, which serves, as in the case of the tunnel-kiln, for the reception of the trains of cars. Of these trains every car is provided with racks which serve for the reception of the bricks to be dried. The cars are loaded with the bricks coming fresh from the machines, shoved into the tunnel at the chimney-end, as in the case of the tunnel-kiln, and removed at the end opposite from the dried bricks. The forward movement is made by some pressure-apparatus which, however, has to exert less power in this case than in that of the tunnel-kiln; as, on account of the low temperature that prevails in the drier, no sand-grooves to exclude the wheels from the floor space are necessary, and moreover a lubrication of the wheels seems allowable. The floor of the drying-tunnel consists of iron plates, immediately over which the track runs, and which plates at the same time form a cover for a heating-channel that lies under the drying tunnel. The furnace that heats the drier is situated near the end of the drier-tunnel opposite to the chimney, and consists of a grated fireplace adapted to the fuel to be used for the heating, or a gas generator. The fire-space is overarched to a brief extent with fireproof bricks; thence the products of combustion pass under the cooled off and escape into the chimney. The fire-gases, therefore, do not come into contact with the clayware to be dried, but the developed heat is communicated to the iron plates that form the developed heat is communicated to the iron plates that form the floor of the tunnel, and from these is radiated to the bricks. By this arrangement of the firing, it is obvious that the temperature is lowest at the chimney-end of the drying-tunnel, and therefore at the place where the green bricks are brought in. The motion of the air, which has to carry off the watersmoke developed from the bricks in the drying-tunnel, takes the direction opposite from that taken by the hot air from the fire. The former air enters the tunnel at the same end where the green bricks are shoved in, and therefore takes the same direction as does the train of cars; whereas the fire-gases used for heating continue under the iron plates of the floor in the opposite direction. Thus the air, which in its passage through the drier keeps entering hotter regions, can be prevented from giving up again the steam it has once absorbed; and in its steady progress through the higher temperatures it continually meets with, it can absorb and carry off an ever greater quantity of steam. By the time the air has reached the place where the temperature of the drier-floor is highest, that is over the fireplace, then the air has attained its highest temperature, has absorbed the greatest amount of steam, and is removed once more from the drying-tunnel proper.

For this purpose the top of the tunnel is also overlaid with iron plates, and at some distance above this plate-roof is extended an arch, so that another tunnel is formed in the intervening space. This upper tunnel connects on one hand with the inside of the drier, just over the fireplace; and, on the other hand with an iron pipe which is erected concentrically inside the chimney. This tunnel now conducts the hot, steam-laden air to the chimney and enables it, by condensation, to impart its perceptible and some of its latent heat to the iron plates that form at once the floor of the conduit and the roof of the tunnel of the drier, whence this heat is radiated down to the bricks again. The outflow of the water that condenses in this upper tunnel is provided for with a gentle slope of the iron plates and a small drain-pipe. What steam is not condensed and drained off goes with the air up the chimney. Over the fireplace and the steam-hole just above it in the tunnel roof, the drying-tunnel is extended in a simple manner to give the hot, dried bricks a chance to cool off before they are removed from the tunnel. Both ends of the tunnel are what, as in the tunnel-kiln, amount to intermediate spaces with closable doors for taking in and out the carloads of bricks. The entrance-door is provided with an opening for the regulation of the draft.

Although this arrangement must be regarded as one that, in the matter of utilizing the heat to the best advantage, fulfills the requisites the best of all the drying-apparatus hitherto constructed, yet the question is whether these will be adopted at all in practice; as from the practical point of view of drying bricks and other material, serious doubts may arise. On the one hand, particularly in the case of machine-made bricks, which are generally more liable than handmade bricks to crack under the influence of rapid drying, it must appear hazardous to shorten the time of drying to any considerable extent. Moreover, should the apparatus be generally introduced (for which end the inventor is striving) it must happen in the vast majority of cases that not a single brick, under such treatment, will leave the drier uncracked. This, however, lies in the nature of the clay. If the clay is to dry without changing its form, that is, without cracking, the outer layers must not be made to lose their moisture too fast. This can be accomplished only when the evaporation of the water on the surface is compensated by the capillary attraction from the inside. For such a compensation, however, a fixed, and in many clays a long stretch, of time is necessary; and if one will not wait so long, there takes place, through the greater contraction on the surface, a tension which must lead to warping or disintegration. Even if, in many clays,

the equalization of water from center to surface is such that they can bear, without harm, a more rapid drying than can be accomplished in the open air (and this condition can be left out of consideration in an artificial drying process), yet there is danger in another direction. The heat is imparted to the bricks to be dried, on the one hand, by direct radiation from the iron plates forming the floor and roof of the drying-tunnel, and on the other hand, by the passing through of the air that has been warmed on the iron plates. As the radiation of heat must affect first the outer courses of bricks on the drier-cars, and as the circulation of air must be strongest on the walls, under the roof, and on the floor of the drier-tunnel, because there the circulation finds less frictional resistance than in the inner parts of the enclosure, then the outer, and particularly, the upper and lower layers of bricks must heat faster than the innermost ones, and a certain length of time is always needed to impart to the inner bricks the same temperature as the outer. As the drying will have to be comparatively rapid, if it is to be advantageous to the manufacture, and the quantity of air that can be used for absorbing the steam is very small compared with the amount of air available in open-air drying, then the amount of moisture in drying in the apparatus must be much greater; and it would be difficult even to avoid slight differences of temperature between the surfaces of the outer and inner bricks. Hence the fast-developing steam near the heating iron plates might condense, from time to time, on the surfaces of innermost bricks and thus make them soften or crack. Whether this danger will be avoided in practice, whether still other evils will present themselves in the handling, or whether the heating iron plates will offer a sufficient transmitting surface to radiate into the drying-tunnel the amount of heat requisite for the shorter time of drying, without making the tunnel too hot, practical experiments will have to determine. One must wait until these questions are settled. Only then can it be shown whether this apparatus is of practical significance, even if the theoretical argument for the excellence of the system does seem plausible. And if, after practical experiments, defects appear in the arrangement, then one cannot set these objections aside and make the drier a valuable auxiliary apparatus in the clay industries.

It were well to consider whether this drying-apparatus, which rests on a theoretically sound basis, so far as utilization of heat is concerned, has not much better prospects of success in the cement manufacture. In that industry there are bricks to dry that are meager in the matter of clay, which contain little water and tend to

give up what they do contain more easily and rapidly. Moreover, it is not essential that the bricks keep a strictly regular form; indeed, even if they do crack here and there, the pieces are still useful in the manufacture. Particularly should such a drier prove very useful, perhaps, in connection with dry-pressing, as the cement manufacture succeeds in rendering it useful in modern times.

Brickmaking on the Lower Rhine and in Belgium.

As every industry follows a different line and exhibits certain peculiarities in the various countries in which it is carried on, so it is with brickmaking; and if we discuss the manner and method of producing bricks in Belgium and the Rhine country, this becomes apparent, because there the modes of brickmaking show many kindred points and seem to have borrowed certain usages from each other. The difference is not always owing to the fact that the material demands another mode of treatment from that in other regions, but is rather prompted by the variations of taste, custom, and mode of life which we find in various peoples, and in a certain predilection for particular tools and apparatus once established by peculiarities of climate and conditions of trade determined by geographical relations. When one travels through the Rhine countries, one finds that there brickmaking takes a different position from that it takes as we know it in the greater part of Germany. While we find in brick factories in Germany great plants, manufacturing machines, dry-sheds, store-sheds, and kilns, nothing makes us aware of this industry there—at least in most cases—but a pile of burnt goods or a rubbish heap. Genuine brick plants are to be found only in a few places specially favored by commercial conditions, the bulk of building bricks are produced, however, for a special purpose. If one wishes to erect a house, a factory, etc., the requisite number of bricks are molded on the nearest spot where the clay is suitable, on a level piece of ground in the favorable season, without any outlay for costly plants, sheds, and kilns; set up in rows, and after the bricks are thoroughly dried in a field or in a pile, the manufacture ends. This is almost always the way one makes brick for oneself in country building. This is undoubtedly the method adapted for the improvised sort of manufacture; and if the burn is successful with the help of favorable weather, it is also the cheapest. But in most cases the heavens are not favorable to these burnings in piles, and then very sad results are obtained.

Effort has been made (thank God, without success, hitherto) to introduce this apparently practical method of manufacture in other

countries; and from the absence of this method, there seems to be a desire to prevent a retrogression of our German manufacture, and at the same time to emulate the Oldenburg and Dutch manufacture discussed in a previous letter.

Considering the provisional character of most of the Lower Rhenish and Belgium brick works, as they have, as a rule, to furnish the material for one or a few buildings, it is very natural that one cannot install costly apparatus therein. One cannot avail oneself of pug-mills and soaking pits in order to impart to the clay that degree of homogeneity which is requisite to produce a good building brick, if the paste does not possess by nature the desirable homogeneity; but it must suffice to mix the clay with water by means of a hoe and spade and also by treading the mass underfoot. One employs no dry-house, but leaves the bricks on the ground, where they are spread out until they can be piled up together. They are not sheltered from rain in sheds, but at best are sheltered in the tiers with a cover made of straw or rushes woven through frames of poles. Then, after they are dried, they are immediately packed together in the pile in order, after the pile has reached a certain size, to burn the bricks with coal strewn in layers between them.

The molding is always done in a sanded mold with a strong bottom, and with clods rolled in sand; and for the most part such is the stiffness of the clay that the offborne bricks can be set up on edge at once. It is astonishing what skill the workmen, who engage in brickmaking during the warm season, frequently attain in molding. Often one of them, with one boy to take the brick out of the mold and sand the mold anew, and another boy to off-bear the brick between two little boards, will make 5,000 or 6,000 bricks a day. The molder has also to cut the clods from the clay-pile, roll them in sand, to cast them into the mold, and to cut off the superfluous clay with a wire stretched over a bent piece of wood after the fashion of a violin-bow. After the drying, the bricks are stacked up for burning, mostly in the clay-pit with coal strewn through the pile in layers. Piles of 50,000 to 300,000 bricks are then fired in tunnels made for this purpose at the bottoms of the piles. During the burning, which lasts from a fortnight to six weeks, according to the size of the pile, the draft is regulated thus: the scoving of clay which incloses the piles is pierced in some places or closed up again in others, as the burner finds necessary.

It is clear that such burning is pre-eminently dependent for its success on the favor or disfavor of the elements, and that it can be practiced with any prospect of success only in summer; while

the storms and showers of the spring and autumn months become dangerous and may cause egregious failure. In burning in piles under normal conditions one counts, as a rule, on a loss of one-eighth in melting and breakage; but when unfavorable elemental conditions enter in, a loss of from one-fourth to one-third by breakage is no rare thing, unless one can lay the blame therefor on negligence of the burner.

The character of the bricks made in this way, and the peculiarities of them resulting from their mode of treatment, are such that their exterior is little prepossessing; that most of them show an irregular stony and chonchoidal fracture; that they appear crazed, spoiled by rain, and oblique-angled; and are in most cases smoked up and always void of ring whenever one tries to make up for the lack of homogeneity with a strong burn.

Although we must draw a pretty dismal picture of this transient, unstationary mode of brick manufacturing, it should be brought out that in a few places favored by nature and by transportation facilities brick plants, and often very extensive ones, have been established. Moreover, although the method customary in these countries must remain the same on the whole, yet the conditions here permit of greater care in the manufacture and of the attainment of better contrivances for protection from the harmful influences of the elements. Furthermore, in these plants are manufactured roofing-tiles, almost exclusively S-shaped, so-called Dutch tiles; and floor-tiles, mostly blue-smoked ones, products which demand, as a matter of course, greater carefulness and a share of the better work usually observable here in turning out the simpler product, brick.

The finest brickmaking establishments in Belgium are in the neighborhood of Antwerp on the banks of the Schelde and Rupel. Here brick plants are about an hour's journey apart on the right bank of the Schelde; and in order to give an idea of the extensiveness of the brick industry concentrated here, I will present the following figures of the brick produced by the chief brickmaking corporations in the year 1871:

In Boom and Niel, 200,000,000 brick, besides a few million roofing-tile, floor-tile, and a limited quantity of drain-tile.

| | |
|---------------------|-------------------|
| In Rumpst | 90,000,000 brick |
| In Rupelmonde | 100,000,000 brick |
| In Burght | 25,000,000 brick |
| In Hoboken | 10,000,000 brick |
| In Hemixem | 50,000,000 brick |

The number of large and small brickyards in these places may exceed 100.

The size of the brick made here is considerably smaller than those in Germany; they measure about $7 \times 3 \frac{1}{3} \times 2$ in.

Here the manufacture is the same as in the other parts of Belgium, except that one can avail himself of the advantage of stronger establishments. The fine and heavy clay is always dug from the rising bank of the Schelde just back of the plant, and keeps the bricks standing in rows to dry, sheltered from the rain under open sheds. The kilns are rectangular, overarched spaces capable of holding from 50,000 to 200,000 brick. Therein the burning is done in the same way as we have seen in the case of field-kilns, only without the enormous loss in breakage through lack of shelter from wind and weather and from poor burning.

Several such kilns, usually from four to six, are always built side by side, so that their long sides which bear the abutments of the arches are in contact. The entry doors on one of the main walls are about 5 ft. wide and reach nearly to the top of the arch. On the opposite main wall, close under the arch, is an opening about 2 ft. square which is in connection with a pipe running over the whole row of kilns to lead the products of combustion into a tall chimney erected outside the kilns. In these kilns the bricks are set in such wise that at the bottom are left three channels three bricks high and about 6 in. wide and running the whole length of the kiln; then come three layers of bricks, set closely one above another, then a layer of coal, then three more layers of bricks; and so on up to the top of the arch. The layers of coal are thickest at the bottom and are gradually thinner all the way up, their thickness being determined by experience. When the kiln is filled the entry door is doubly walled up with sand-panel; only at the bottom is left an opening about 12 in. wide and 18 in. high, which serves as a place to light the fire in the kiln and for the admission of the air necessary for burning. As the bricks are packed close together, a very high stack is always requisite in order to produce the proper draft for burning. Such a kiln burns in two or three weeks, according to its size, and turns out a decidedly better product than the piles burnt with layers of coal in just the same way without any outside walling; but here, too, one misses a clear ring in the bricks and can very often observe smoke-streaks in them. The construction of these kilns is pretty costly, and I do not believe I make a mistake in rating the cost of building higher than that of a continuous kiln of equal capacity. The use of simple piles in the larger stationary brick plants, aside from the consequent losses which, after a few burnings, would outweigh the cost of building strong

walls, would be utterly impossible, because the enormous heaps of ruins could not be removed.

If we consider a brick plant with a production of 8,000,000, working with common clamp kilns, then at least 1,000,000 a year must go to the rubbish heap; and such a plant would need a great deal of surplus room in order to get rid of the rubbish that would accumulate in a few years. In such plants, where only one or two piles are burnt for a special purpose, the waste serves in part for leveling the ground again, or in unsandy regions or in large establishments, as in the case of Krupp in Essen, the same is ground up and is then used in making mortar. For the improvement of roads the material is utterly useless, because it consists of soft-burnt clay.

Within recent years a few of the more intelligent manufacturers have also erected continuous kilns; and these have proved their superiority over the old constructions, not only in the matter of economy but also as regards the better quality of the manufactures produced; and if one does not aim here at burning clinker-bricks, like those of Oldenburg, yet one always turns out, with smaller cost of plant and labor than before, bricks better looking and with more ring to them.

Of special importance to the Lower Rhine and Flanders (and therefore deserving particular emphasis) is the manufacture of dark, blue-black floor-tiles and pan-tiles. These are made of the same material as the red tiles produced at the same time, but by a certain so-called steaming-process, which may not be known everywhere, and which gives them peculiar colors and a greater durability. The roofing-tile is S-shaped, and is known in Germany as Dutch tile and is widespread in other parts, as in Hesse and Thuringia.

The kilns for burning roofing-tile are long rectangular ones, 33 ft. long, 13 ft. wide and 11 ft. high, and are overarched. In each main wall are three openings with closable iron fire-doors. These openings correspond to three grates extending throughout the length of the kiln. These grates are fed with coal and therefore possess ash-pits. The grates, formed of cast iron grate-bars, are 12 in. wide and have joints of about 2 in. On the roof is a row of 15 flue-openings for the smoke-gas. Every third one opens into a common channel running over the kiln-roof and sends the fire-gas off into a main channel connecting with the chimney.

The process employed for burning the roofing-tile or common building brick blue, or for steaming, in this kiln is the following. As is always done in burning roofing-tile, the lower part of the kiln is set full of bricks and floor-tiles. Into these are made the stoking-passages, which are projected in the usual manner. The bricks and

floor-tiles are set about a yard high. Then come the roofing-tiles, set upright, with the different ends alternating up and down and the individual rows crossing one another right and left. To avoid as far as possible any shrinkage and resetting of these tiers and consequent distortion, poles are laid across in the tiers about a yard apart. When the kiln is full the contents are burnt as if it were intended to burn the tiles red. When the kiln is heated enough the flue running over the kiln-roof is removed from the flue-holes that open into it, and all but two or three of the openings are stopped up very carefully with bricks and clay. Then into the stoking-passages below is thrust fresh-felled alder-wood, 18 logs per burn in a kiln of this size; and now the fire-holes as well as the ash-pits and the last of the flue-holes above are scooped over as quickly as possible and made air-tight.

Through the effect of the heat on the green wood, gases now form in the mass and a dense vapor fills the whole kiln. These gases are not combustible, as they are deprived of the air necessary therefor; and they now act on the clay so that, at the expense of the oxygen which the iron oxide containing the same might give off, they burn and transform the red-coloring iron oxide combinations into black-coloring combinations of iron protoxide.

When this process, whereby the clay receives the black-blue color, goes backward so that the development of the gas issuing from the wood ceases and fresh air can enter through the unavoidable cracks in the kiln, then one tries, after putting in the wood, to cool off the kiln as suddenly as possible and to develop steam in it, pouring water on the roof. To avoid the direct influence of the water through cracks in the kiln, the sand covering the roof to a depth of about 7 in. is moistened by sprinkling and firmly packed. Then between the openings in the roof and the abutment are erected little dams of fresh clay; and now water is pumped or carried up until it stands a few inches deep over the roof, and by the continual oozing through the porous arch-bricks a steady development of steam is kept up on the inside of the kiln which counteracts the entrance into the kiln of outside air. From the foregoing it will be clear to everybody that the solidity of the kiln and particularly the crown must suffer extremely from such a source of strain; and therefore it seems inevitable that the kiln must be subjected twice a year to a general repairing in the way of renewing the crown.

The roofing-tile steamed in this way show less tendency to disintegration than the red tile, and therefore the high council of the city of Ghent has ordained that all roofs which are turned toward the streets shall be covered with nothing but blue roofing-tiles, and

it allows the use of red tiles only for the rear parts of buildings and the sides of roofs sloping towards the yards.

The exclusive use of alder for the process described seems not absolutely necessary. There are substitutes which are capable of producing a great quantity of gas working in the same way. If, for instance, the operation of the same could be made up for by the dropping in of coal-tar after the kiln is closed air-tight, then the sudden cooling off of the kiln can be better accomplished in another way than by wetting the roof, the weakest part of the structure. By squirting streams of water into the kiln itself at a less dangerous place, perhaps in the ash-pits of the fire-vault, this could be done better. In this particular it goes no better with the Belgian brick industry than with the German. In both countries there is a tenacious clinging to the processes inherited from one's ancestors and a surpassing ignorance of one's business; and whenever anybody thinks of and tries an improvement the chasms of a defective knowledge present themselves and frighten away the other, and perhaps better, idea.

On Oldenburg Clinkers.

Not every district is so blest by Nature that a man must use the same materials that are produced from it for building his dwelling as he does for paving his streets. In mountainous regions building stones, which fulfill in a greater or less degree the requirements in firmness and incapability of disintegration, are obtainable everywhere without difficulty. In one locality there is sandstone; in another there are slate, basalt, granite, limestone, and whatever they call all the forms of rock that supply building material. The unmountainous low country of northern Germany has its erratic blocks; the coastland of the Baltic Sea has, in many places, its flints; and there one uses what lies nearest. But there are also districts which are utterly destitute of these materials; their fields, marshes, and heaths lack even the erratic blocks which are needed for paving the streets of the cities and villages.

This lack must be made good by artificial means. Here, then, to fill this gap, brickmaking, with its best and most durable products, is naturally called on in the first place; and we see that in just such districts the manufacture of brick reaches its greatest development. In looking over all Germany, we find that wherever nature provides good building material the poorest brick are made; whereas, where firm, hard rock-forms are lacking, clinkers must take their place. Indeed, these make up for the lack as well as one could desire.

In such regions, where the burnt brick has attained the predominance over the natural rock, one naturally makes higher demands in durability on the building brick. There one does not know how lumps compacted of clay and stone are made into bricks, as we can see them so manifoldly in our blessed Germany in all stages of the preparation of the material and burning. Here the only thing valued as brick is that which in firmness equals the best stone and which surpasses it in resistance to the influences of air, water, frost, and sunshine—the clinker. The home of the manufacture of clinkers is the coast of the North Sea, Oldenburg, Friesland, Holland, a tract of country which has no natural building stones at all to show. On the other hand, it has widespread deposits of beautiful, fat, iron-bearing clay. One cannot, by any means, place the clinkers produced here in comparison with those which are called clinkers in other parts of Germany. Moreover, these products are, almost without exception, produced unintentionally; their appearance is brought about by accident due either to the method of burning or to the construction of the kiln. Only in single instances is a clinkering accomplished designedly; namely, whenever the raw material is of such a nature that it takes no bond without a thorough slagging.

In the Oldenburg coast regions, however, as in Holland, brick manufacturers pursue a totally different aim. Here, in all cases, the sole intention is to produce great quantities of clinkers; while that product which, in other parts of Germany, one would mark as stock-brick, remains quite unnoticed and passes as a necessary evil in the manufacture. Furthermore, one must take into consideration that here the clinkers have not only to supply the material for house-building, but are used most extensively for causeways; a use which demands the greatest durability. Whoever does not know such a street and has never traveled over one, can form no idea of the ease with which, even in the most unfavorable weather, loads can be moved along on one, and would be astonished at the smoothness of the road and the absence of holes and deep ruts, such as we are familiar with in our best stone-paved streets, to the sorrow of the mail-coach passengers.

A clinker used for such a road is, however, something quite peculiar. Generally, one is not accustomed to work the clay too thoroughly. As a rule, one considers only this: The main thing in a brick is its outside appearance; how it looks inside is to the manufacturer and consumer alike a matter of course, because all are made the same way. Whenever an especially durable brick is desired, one has to destroy by a stronger burn, the lack of homogeneity of

the mass which weakens the cohesion. It is thought, however, that this homogenizing is never thoroughly accomplished in this way, and therefore the Oldenburg brickmaker tries to bring the firmness, which the brick obtains in the strongest fire, to the highest point attainable by means of the tempering wheel and pug-mill. By such a process only is it possible to get brick of such imperishableness as is the case here; and if one compares the durability of causeways paved with them with those causeways on which are used the hardest natural stone, as granite and basalt, then one can get an idea of the stability and indestructibility of the clinker.

The clinker-paved streets will last 15, 20 and even 25 years without needing repairs; whereas it is well known that other causeways will endure only a very short series of years without fundamental repairs in the shape of ballasting.

But it is not only for streets that one requires a thoroughly durable material. One makes the same high demands on the usual brick for building in Oldenburg. It is a pleasure to go through the stately villages with their high-gabled, clinker-built houses. A plaster roughcast on the houses is nowhere seen; indeed, it were useless, as these easily obtainable brick are applied for a protection against elemental influences.

As for the technique of producing clinkers, it does not differ from the general method of brick manufacture, except greater value is set on careful preparation of the clay and on getting the hardest possible burn than is set elsewhere. Therefore, the use of the tempering wheel and pug-mill is much more extensive here than in brick plants of the same capacity in other districts. Hence, the clay is more completely homogenized than is elsewhere deemed necessary.

The burning of clinkers is done with turf, obtainable only here, and in most cases, especially in the innumerable smaller plants, in old-fashioned, partly open, but mostly overarched kilns in enclosed sheds. However, in the large establishments in the neighborhood of Oldenburg and of Jahdebusen, there are about half a dozen continuous kilns, which turn out the most excellent goods this burning apparatus is anywhere capable of producing. As, in making material that has to meet the highest requirements, brickmaking stands, in the districts in question, on a higher plane than almost anywhere else, and this branch of industry is carried on there with such intelligence as it is, perhaps, in few other places, so has the continuous kiln there demonstrated most clearly its superiority to all other kilns, not only in fuel-saving but also in uniformity of burn. When it gives the greatest satisfaction where it must fulfill the highest re-

quirements, and the brickmaker looks with pride on his kiln and with contempt on other imperfect apparatus, and can with pride challenge the writer of this to mention a brick plant anywhere in Germany that can turn out just as good or better products in continuous or other kilns, it is certainly a good argument for the serviceableness of the continuous kiln in burning clinkers.

The accomplishment of such things demands intelligence, and whoso would see how a brick plant should be run let him go to the North Sea-coast of Germany and take example.

The Influence of Sulphuric Acid on Glazes and Pastes.

Hitherto, the harmful effects of sulphuric acid on glazes, enamels and pastes have been quite disregarded. It is customary to form glazes of lead-oxide, alkalis, lime, alumina, boracic acid, and silicic acid. Nobody has ever thought of the fact, however, that sulphuric acid is also a constant ingredient of glazes. One forms pastes of kaolins, plastic clay, feldspar, sand, lime, bone-dust, etc.; sulphuric acid, however, is vouchsafed no notice therein. Yet in both cases it is of importance; and however limited the amount, its presence must be taken into consideration.

Of all the salts that, intentionally or unintentionally, enter into the glaze mixture, the sulphates are the hardest to dissolve. The acids formed from organic sources are very easily destroyed. Carbonic acid and nitric acid are expelled in the fritting; chlorine, bromine, and iodine are destroyed, with comparative ease with the aid of steam; chromates and manganates are likewise easily decomposed, where they can be formed; only sulphuric acid gives the flux a longer resistance. In manuals it is stated, indeed, that silicic acid drives out sulphuric acid. This, however, does not take place completely. The decomposition is complete only in the presence of reducing influences, or at a much higher temperature than glazes and frits are, as a rule, heated to. Pelouse has indicated that plate-glass fused from sulphate of soda may gather 3 per cent of undecomposed sulphate of soda without losing any of its transparency. It shows only a frostlike efflorescence which, as often as it is rubbed off, reappears after a time. One can observe a like peculiarity in stoneware glazes; especially in those containing much protoxide of potassium, and here this peculiarity is owing to a similar cause at bottom; whereas, the sodaic glazes show the peculiarity less. However, this power of the glass to free sulphates is not uniform, but varies according to the composition of the glass. One bisilicate that, with a mixture of sulphate, I fused, showed a content of 4 per cent of sulphuric acid; a trisilicate, fused at the same tempera-

ture and under the same conditions, showed only 2 per cent. It follows that a bisilicate mixed with sulphuric acid, when changed to a trisilicate through absorption of silicic acid, releases 2 per cent of sulphuric acid in the form of sulphurous acid and oxygen. Indeed, it happens that the clearly fused glasses gave to the body, namely in contact with silicic acid, quite foamy pastes. In reality, this action might be the most frequent cause of bubble-formations, of boiling up, when it enters strongly; and of egg-shelliness of stoneware glazes when it enters slightly. And this is an exceedingly important action; an action which explains many times the appearance of bubbles; for from the usual constituents of the glaze we can derive absolutely no bubbles.

Now let us see whence the sulphuric acid arises in the glazes, how it works, and how we have to offset its effects; and let us consider one by one the sulphates in the glaze, in the paste, in the water, and in the fire-gas.

1. In the Glaze. The glaze materials always contain greater or less quantities of sulphuric acid. White lead and red lead, especially the latter, often contain several per cent of it. Soda, with the exception, perhaps, of the so-called ammoniac soda, much used in latter times, always contains sulphuric acid. The same is true of potash. Saltpeter is for the most part free from sulphuric acid, as is borax. On the other hand, boracic acid always contains a few per cent of sulphuric acid. Sometimes lime, or even barytes, is added as a sulphate in the form of gypsum or heavy spar; although this is not only technically wrong, but also without advantage, economically. In fritting, sulphate of lime and sulphate of baryta exchange with the alkali salts; sulphate of alkali is formed, and the lime or barytes goes into the glaze. On the other hand, the sulphates of alkali, so far as they are not released unchanged by the frit, rise to the surface as glass gall. In this way one preserves a frit saturated with sulphuric acid, and besides loses in alkali that is simply washed out. Now if the frit is intimately mixed with sulphates, and sand or clay, materials containing silicic acid, which form an acid glaze, are further added, then occurs an expulsion of the sulphuric acid, and therewith a development of gases which turn the glaze from an eggshelly to a vesicular character. Often another secretion of gall takes place on the surface, overspreading the same like a layer of fat and making it opaque. These phenomena are most striking when the glaze is burnt in the muffle; less so in the kiln. This fact is owing to two causes. In the first place, if the burn progresses rapidly in the muffle, the bubbles have not time to rise to the surface, there to burst and smooth themselves out

again. Secondly, as a rule, an oxidizing atmosphere reigns in the muffle; whereas, at times, in the kiln a reducing atmosphere reigns. The production of a reducing atmosphere is the only sure means of removing the sulphuric acid from the glaze and of obviating the appearances connected with it; a means which certainly must be used with prudence. Thereby the sulphuric acid is easily removed in the glowing heat, as it is reduced to the unstable sulphurous acid; whereas in the oxidizing atmosphere it is very stubbornly held back. When the muffle is heated to so high a temperature that the glaze forms a smooth surface, I shove some resinous wood through the peephole, and thereby fill the muffle with a thick fume. This is repeated two or three times. Naturally the operation cannot be undertaken until the glaze completely covers the colors and so protects them from the effects of the reducing gases; otherwise, the colors susceptible to reducing influences, pink, antimonial yellow, etc., would vanish. With prudence, however, it is possible to retain even such colors as can be easily destroyed by reducing gases. Also, in the employment of lead glazes, the reduction may not be effected too intensely or continued too long, or a blackening of the glaze takes place. In this connection it is to be noticed whether the lead oxide is contained as such in the glaze, or whether, fritted, it occurs therein combined as silicate of lead. Free lead oxide is much more easily converted into metallic lead by reducing influences, than silicate of lead. I have always been able to undertake the above described operation without harm with fritted lead-bearing enamels on porcelain. The sulphuric acid content seems less hazardous, indeed, quite unhazardous, in a porcelain glaze. Therein it is always burnt to a higher temperature with a strong reducing flame and the sulphuric acid is thereby completely destroyed and expelled. It is, therefore, permissible to introduce lime, in the form of gypsum, into the glaze. This has its advantage in the molecular structure of the gypsum. For this reason the glaze is more applicable, in many cases, than in the employment of marble or limestone.

2. In the Paste. The clay used for making the paste frequently contains selenite, iron pyrites, or other sulphur compounds. In slumming, the selenite is dissolved in water, makes an exchange with magnesia-bearing materials, and gives sulphate of magnesia; and this salt impregnates the paste with sulphur compounds. From iron pyrites proto-sulphate of iron is at first formed in the bed of the paste. Then this undergoes changes with the constituents of the clay to alumina, magnesia, or sodium carbonate. Often these salts thus formed become so strong in the paste that they stand out as visible efflorescences, especially at the edges. How to remove

such efflorescences Dr. Wilkens decided recently; it is done with chloride of barium, or better, with Witherite. With the removal of the efflorescences, however, the sulphuric acid itself is not expelled from the body. It remains finely dispersed therein as sulphate of barium. The sulphuric acid in the body, on account of its insoluble condition, requires for its expulsion a much higher temperature than does the sulphuric acid contained in the glaze. In brick-clays, which are comparatively easy of solution, the expulsion does not take place under reducing influences below the melting-point of silver, and is accomplished only when the clay is fused. In the relatively more fireproof materials of the stoneware and porcelain industries, the sulphuric acid is always expelled at the correspondingly higher temperature. In brick-clays, even when the clay is in flux, the sulphuric acid can, however, remain under oxidizing influences. After the biscuit-burning, therefore, no inconsiderable quantities of sulphuric acid are present in the paste, which are released by the water used in the glazing and restored to the glaze. I have made the observation that bodies that have been burnt exclusively in the reducing flame (stoneware bodies) always yield a glaze more eggshelly and bubbly in character than those bodies in which at a higher temperature, the melting-point of gold, a reducing atmosphere is employed now and then in the kiln.

However, the clay does not merely contain sulphates within itself, but the same are imparted to it also from without in the throwing. As is known, the throwing is done in gypsum molds which are pretty easily damaged. At the completion of the throwing, little particles of gypsum remain adhering to the clay. Then in the washing these particles are worked into the clay. Out of the molds also comes the addition of a water solution of gypsum. Now if these bits of gypsum remain in the paste they can give rise in the porcelain to a peculiar phenomenon,—pock-marking. Under oxidizing influence (and pock-marks arise only in the oxidizing flame, never in the reducing flame) sulphate of lime can maintain itself undecomposed until the body is thoroughly condensed. Just when the fluid constituents are included in the body the reaction with the expulsion of sulphuric acid begins. I have demonstrated this fact by synthetic experiment. Indeed I should not know from what other source a development of gas could come into the paste in the oxidizing flame. In the reducing flame the sulphuric acid is expelled before the body has acquired a close texture.

3. In the Water. In the water used for tempering the glaze, we find a further source for the entrance of sulphuric acid. Particularly momentous can this become in the stoneware industry; less so in the porcelain industry, because there any sulphuric acid can

always be removed by the reducing flame, especially when the acid happens to be finely distributed in the glaze and paste. In the shifting to new places I observed that all the stoneware glazes were bubbly, and that the pieces were not to be used. On closer examination I found the cause in the water employed. In the environs of the well in use were accumulations of old molds which imparted to the water a good deal of sulphate of lime and sulphate of magnesia. By the use of rainwater the evil was immediately done away with. Therefore one has to pay particular attention to the quality of water used.

4. From the Fire Gases. In employing anthracite and lignite coal the fire-gas, as is known, always contains considerable amounts of sulphuric acid; therefore, the water formed in the firing has always an acid reaction, partly of sulphuric acid and also, when the fuel contains common salt, of hydrochloric acid. When the kiln and setting are very cold this water often falls in considerable amounts, particularly in those parts of the kiln where the air stagnates. This acid character of the water of condensation causes a peculiar phenomenon, the passing through of colors. The acid water is precipitated upon the pots and dissolves most of the colors; as, cobaltic oxide, manganic oxide, chromic oxide, etc., and drives them to the other side of the vessels. With the evaporation of the water of condensation, the coloring metallic oxides resettle themselves, and thus a perfect reproduction of the coloring on the outside of the vessels often appears on the inside of them.

I might add, by way of conclusion, that the sulphates are also frequently imparted to the vessels by the colors used. If the colors are not sufficiently washed out and still contain sulphates, then an eggshelliness or a bubbliness often appears over them, or even a complete devitrification of the glaze takes place in consequence of separation of glass gall.

The Manufacture of of Black Clinkers.

One branch of English brick-making, which has come to be of great importance in that country, but which seems to be as yet quite unknown in Germany, is the manufacture of black clinkers. Efforts are being made at the present time to bring these bricks into general use in this country also.

In Germany, as well as in England, the architect needs a black material to produce certain contrasts in facades, but the material furnished by the brick-maker for this purpose is so different in the two countries that it is worth while, I think, to examine into this difference and see whether we cannot derive some profit from an understanding of the English process.

The bricks used to adorn facades in this country are prepared by boiling ordinary facing bricks in coal tar. These dipped bricks, as they are called, are of course made much more durable by being saturated with the tar, which protects them from the influence of the weather, but the dust soon gathers on them and they become unsightly; the black color, so deep and lustrous at first, changes in time to an ugly, dull gray. Since these bricks dipped in tar can be manufactured at slight expense, they are extensively used in England also, but in the more ornamental brick-works they are never employed; a material is used instead which is not only far more beautiful and durable, but seems, in fact, almost indestructible. In mediaeval architecture in this country the same effect was produced by the use of bricks covered with a dark lead-glaze, which were offensive to the eye on account of their glistening surfaces. The English products occupy, as far as appearance is concerned, an intermediate position between these two varieties.

The reader will perhaps remember that in an article on brick-making in Belgium, the manufacture of black tiles and bricks was mentioned. A similar process is in use in England, but in the latter country the effect of the dark color is heightened by a very thin glaze, with a faint black luster, quite different from the smooth shining surfaces we are familiar with.

These bricks which I am about to describe—the blue Staffordshire bricks, or iron bricks, as they are called, on account of their appearance and hardness—are manufactured in the center of the Staffordshire Pottery Works, and in the south at Bishopton, near Southampton. The clay used here contains some iron, but otherwise stands firing very well. The bricks made from this clay resemble most nearly in appearance the material known in Berlin as Rathenow bricks, or the bricks made in the coal beds of Laarbrücken from the clay obtained by exposing red sandstone-grit to the air. The bricks are generally made of clay which has been prepared with great care and usually washed. The better products of this sort are always repressed, to make the surface firmer and more lustrous. The bricks are burned to the hardness of clinkers either in the Staffordshire kilns, which I have described before, or in smaller ones similar to them, round arched kilns about 3.5 meters in diameter and 2.5 in height. Six fire-holes are arranged in a circle, and from four to six little chimneys are erected on top of the round arch to make a draft for the fire. The bricks are stacked in such a way that six alleys run from the fire-holes to the center, where they unite in a shaft rising perpendicularly. The surfaces which are to become black are always left exposed. Thus, if the bricks are to be used in mason-work,

they are laid flat upon each other; if they are to be used for paving sidewalks, they are set on edge, always so that the surfaces which are to be exposed when the bricks are used are uncovered in the kiln.

When the heat in the furnace has become so intense that the bricks have reached the state of hardness necessary in clinkers, a few shovelfuls of salt are thrown into each alley. This evaporates instantly in the great heat and covers the exposed surfaces with a very thin, hard glaze. At the same moment fresh coal is thrown into the furnaces, and just before it comes to a glow the fire-holes and smoke exits are closed and sealed. The smoke produced in this way in the furnace has the same effect which we noticed in the use of alder wood in smoking tiles in Belgium. The reduction of the iron blackens the clay to the depth of several millimeters, and this blackening, aided by the flux from the fumes of salt, produces on the surface of the brick a thick, hard coating of the color of graphite, with a dull luster, and makes the exterior completely weather-proof. This process is employed not only for products which are to be used in brick work, for the sake of their color, but the hardening and glazing of the surface is also extensively used with those whose chief purpose is to resist atmospheric action and mechanical wear, i. e., especially roof tiles and paving blocks.

The Manufacture of Bricks from Pulverized Clay.

In a previous article I have described the process of making bricks from dry pulverized clay by means of strong pressure—a process which has been very generally introduced into the central part of England. In taking up this subject again my purpose is not so much to review and supplement the description of the mechanical process, as to draw some conclusions from it. I wish to emphasize the underlying principles of the work, to ascertain what wants were supplied by the introduction of a manufacturing process entirely new to us, and finally to raise the question whether the same reasons which caused a departure from old established methods in the sister-industry in England do not exist in Germany also.

Attempts have been made in this country also to introduce such modifications in the process of manufacture as will enable the brick-maker to get control over those properties of the material which make it particularly difficult to manipulate or involve great expense in certain stages of the process, or occasion the ruin of products in various states of completion, yet, with a few excep-

tions, these experiments are, on the whole, to be considered as failures.

It was partly with a view to surmounting these difficulties in the process and reducing the expense, and partly for the purpose of getting rid of the disadvantages of hand labor and the hand laborers themselves, that all the machinery now used in brick-making has been introduced, and it is unnecessary for me, I presume, to rehearse the mournful tale of the failure of the machines, in many cases, to perform the work which might reasonably be expected of them.

In that very branch of the industry in which such great progress has been made in England for more than a decade, the experiments made in Germany have been unsuccessful and have been abandoned, for there is, I dare say, scarcely a brick plant in Germany where bricks are still made of lean clay in the moist condition in which it is obtained from the earth, although this has often been attempted.

The reason usually urged as an excuse for the less advanced stage of the industry in Germany, as compared with that in England, is that industrial and intellectual conditions in general have been of late years on a lower plane in the former country than in the latter; but this does not fully account for the circumstance. The failure of this industry is due rather to the fact that the producers have possessed a very low degree of intelligence, and the consumers have been too easily satisfied with an inferior grade of artificial building material.

In order to overcome the difficulties connected with the proper preparation of the material before it can be successfully molded and fired, and also, with mistaken ideas of economy, to save the expense involved in this operation, this part of the process has either been entirely omitted or has been carried out only as far as was necessary to produce an oblong rectangular block of burned clay, not a durable weather-proof brick.

This method of manufacture has always found warm supporters in the manufacturers of machines, since it enables them to hold out the alluring claim that their machines can make bricks at very slight cost from the raw earth without any preparation. This is perhaps excusable in these men, but not in those who work constantly with the material, who ought to know its properties too well to be deceived by such seductive advertisements.

In visiting English brickyards one is struck immediately by the difference between the practice which prevails there in the use of machinery to take the place of hand labor, and that which is in vogue in our own country. In England machinery is employed to

prepare the material, to reduce it to a homogeneous mass, while in Germany this preparation is much less common, and where it is undertaken machines are little used for it, or those which are in use are conspicuous from their failure to do the work.

In the German process of manufacturing bricks from clay not moist enough to be molded, the aim has been to save labor as much as possible by pressing the material in its raw state into bricks, and indeed it seems hardly possible to do this in any other way where hand labor alone is employed without the aid of machines. In the English process, on the other hand, the necessity of thoroughly preparing the material has been fully recognized, and this ought to serve as an example to us.

It is true that in England a material is frequently employed in brick-making which our brick-makers would declare entirely unfit for use; it is used there for facing bricks, and it is due solely to its careful preparation that a material can be utilized which is so difficult to handle with our process.

We may perhaps assume that the whole process of manufacture has reached its present stage of development because a material no longer existed which could be worked by the old process. The advantages of the new method were so obvious that it was later employed even with plastic materials, which were of such a nature that they could have been worked by the old established method in a plastic condition.

The raw material employed in this industry is usually a slate-clay of coal formation, which is incapable of being reduced of itself to a plastic mass, and must therefore first be pulverized and then subjected to a long slow action of water in order to be converted into a mass in any degree tenacious. It can, to be sure, be rendered thoroughly plastic by atmospheric action, yet this requires such a long time that it is impracticable in a large industry. Besides, the climate of England is such as to make the success of such a process very uncertain. It is not even customary in all parts of the country to expose ordinary clay during the winter. The winters are not cold enough to insure a thorough freezing of the clay obtained in the autumn, and the summers are too damp to admit of a thorough sun-drying in its stead, so machinery must be employed here to accomplish that which in other countries can be performed by the weather. This accounts for the more general use of machinery in the preparation of the material. But if we reflect how few the means are which nature furnishes without expense, or at less expense than is possible with the application of mechanical power, there would seem to be greater need for the latter than is commonly supposed.

We see, then, that the materials to which this method was first applied were those which do not possess cohesive properties in any high degree, and which offer such resistance to molding that ordinary methods had to be abandoned at the outset. New conditions gave rise to new methods differing widely from the old ones, and the process which originated with these materials was later applied to all others.

In this case the material cannot be reduced to the necessary state of homogeneity by manipulation in a more or less softened or plastic condition, but must be pulverized in order to secure sufficient mobility of the molecules. In order to be thoroughly pulverized the material must of course possess a certain degree of dryness, yet here, too, the difficulties are ordinarily overestimated. The two machines chiefly used in this operation—the crusher and the disintegrator—operate in different ways, and therefore are to be adapted to the properties of the material. The crusher, with its plates, cannot crush oily, plastic clay, or at least not unless it is almost perfectly air-dried, but it pulverizes slate-clay, lean clay and all substances with slight cohesive power, even if they are quite moist. The disintegrator, on the other hand, with its hammers striking in quick succession the particles of material suspended in the air, can crush even fatty clays in the moist condition in which they come from the dry pits.

This treatment of the clay has practical advantages. The stratified structure of the clay, due to its formation by water deposits—which offers great resistance to all softening agents, especially when streaks of foreign matter are present—is completely broken up by this pulverizing. A degree of homogeneity can thus be obtained far in advance of that secured by any other means hitherto employed. Another advantage not sufficiently appreciated is that all impurities, roots, stones and bits of marl, which have escaped complete crushing, can easily be removed by a screen. This sifting has never been successfully performed when the clay was worked in a moist condition. It was these considerations which led to the adoption of pulverization in those industries in which clay has to be worked up while moist—e. g., the manufacture of glazed earthenware, pipes, gas retorts and all terra cotta products.

When the object of the pulverizing is not merely to facilitate the reduction of the clay to a plastic, homogeneous condition, but also to furnish the material for products which are to be made from powdered clay by strong pressure, the greatest caution must be observed in the later stages of the work to prevent flaws in the finished products.

Since the minutest particles of the softened clay cohere, when a

liquid cement is applied the degree of plasticity of the clay in this condition exerts a great influence upon the firmness of baked as well as air-dried products. Difficulties arise when there is an entire absence of plasticity, since the cohesion of particles usually caused by moisture must be produced in this case by enormous pressure.

Still the pressure has no effect if the powdered clay is perfectly dry. A little water must therefore be added, just enough to cause the cohesion of the molecules of clay; but not enough to prevent the reduction of the clay to a tolerably fine powder; i. e., the clay must be in a clammy condition, so that, by the application of greater or less pressure, it can be balled but not kneaded.

And yet it seems that the most powerful pressure cannot cause such perfect cohesion of the molecules as can be produced by moisture. This is less apparent in the air-dried than in the slightly baked bricks; the latter seem to be more susceptible to destruction by atmospheric action than any other kind of bricks, since they crumble into the minutest particles under this action.

A second factor is therefore needed to produce the requisite tenacity. This is found in a more or less thorough clinkering, a softening by burning, by means of which the smallest particles are cemented together. Although this operation is usually quite difficult, it can be performed with safety here since the enormous mechanical pressure already applied has caused such compression that the shrinkage in drying or burning amounts to very little or nothing at all, so that even if the heat is increased to partial smelting there is much less danger of warping than in the case of products molded when wet, and therefore porous at the outset.

The bricks therefore made by pressure from pulverized clay require unusually hard burning, if they are to be rendered quite weather-proof, but in spite of this their shape is so perfect, and the faces so smooth and even, that they will bear comparison with any other article manufactured for this purpose; in fact, they cannot be surpassed in finish by any other product.

But an especial advantage of this process, aside from the production of bricks of perfect shape, is the fact that the green bricks are so firm as soon as they are shaped that they can be handled without receiving impressions. They can therefore be put into the kiln at once. Thus the whole extensive and expensive drying apparatus can be dispensed with, and the whole process made independent of climatic conditions.

This is perhaps the greatest advantage of the process, and one that will be appreciated by those who understand what extreme caution is needed in drying, and how unfavorable weather may

imperil the success of the whole process; besides this, there is no great difference in the cost of the process in winter and in summer.

Anyone who has seen how little space and how small a force of workmen are needed, cannot help being prejudiced in favor of this process, even though it cannot be denied that it has some drawbacks.

One might suppose that if the bricks are put into the kiln before being perfectly air-dried, a harmful effect might be produced upon their color, and the advantages of the process thereby be offset; but it seems that all difficulties can be met here, too, providing caution is exercised in smoking and time enough is devoted to it. At least in several plants which I visited the difficulties encountered in this regard at the outset seemed to have been overcome, even where annular kilns are used, where complaints of this sort are often heard.

Perhaps, too, the smoothness of the faces of the bricks tends to prevent the formation of flaws, for they come out of the steel plates of the press as smooth and shining as if they had been polished. I must remark here that three dampers were always used in smoking in an annular kiln, a luxury not indulged in in Germany, where the firing of facing bricks in annular kilns is altogether dispensed with on account of the trouble connected with it.

My object in calling attention to this subject again was not that I wished to recommend the process as a universal means of securing a well-regulated industry. There is in Germany, as well as in England, plenty of material which requires a treatment adapted to its peculiar properties, e. g., that which needs cleaning, for cleaning can be much more easily accomplished when it is pulverized; secondly, that which has so little plasticity or is so full of foreign matter that it resists molding, and finally that which exhibits such remarkable capacity for shrinkage, and is so affected by the action of air and heat that it cannot be worked in a plastic state. In my opinion experiments with such materials would lead to just as brilliant results as those secured in England. It is certainly worth while to keep this matter in mind.

A Contribution to the Better Knowledge of Kaolin Clays.

In the numerous analyses of kaolins which have been made by Forchhammer, and later by Brogniart, and Malaguti, the chief purpose was evidently to throw some light on the production of clay from feldspar or from primitive rocks, and by ascertaining

the chemical composition of the kaolin clay to discover the processes by which this clay can be obtained as a final product from disintegrating feldspathic rocks.

The chemical means employed in these analyses evidently had in view the separation of the clay from the other materials combined with it, leaving the latter to be reckoned simply as foreign or confusing factors to be disregarded so far as possible in the investigation.

The presence of these foreign elements must be looked at in a different light when kaolins are employed for manufacturing purposes. For here a very important part is played by the fragments of rock which are found in connection with the kaolin and which cannot be entirely removed by the washing process, however thorough that process may be. These fragments of rock need therefore especial consideration. In practical use the kaolins which come from different localities exhibit fundamental differences. Evidently we should inquire into the cause of these differences, since as a result of the investigations mentioned above, the essential constituent of the kaolins, the clay, has, as has been indicated in the preceding article, the same composition in all or nearly all of them. Now, what is the cause of the difference in fatness, in shrinkage, in color, in fusibility, etc.?

We shall approximate a solution of this problem if we first endeavor to determine the nature of these admixtures of kaolin clay and the extent to which they enter into the manufactured product and modify its character. The minerals admixed with kaolin clay in its native state are principally quartz and feldspar or feldspathic minerals.

Since it is not practicable to separate by analysis the feldspar from similar silicates, we cannot do otherwise than class them all together as feldspar—a classification which is, to be sure, not strictly accurate, but is sufficiently so for our present purpose.

Let us assume, then, that it is only with quartz and feldspar in connection with kaolin that we have to do. By so doing it is possible to determine more exactly the composition of the kaolin clay and thereby gain some valuable information as to its behavior while undergoing the process of manufacture, as well as to gain some light on the varying composition of the pastes made of different raw materials. With this end in view a considerable number of specimens of kaolin from various localities were taken in the washed condition just as they are used in commerce and analyzed with reference to their composition. Three of these specimens were from the vicinity of Pilsen: Ledez, Kottiken and Tremosna, others were from Zettlitz, Lettin, Kaschkau, Sennewitz, and

TABLE A.

| | Kaolin from Ledez. | Kaolin from Kottiken. | Kaolin from Tremoesna. | Kaolin from Zettlitz. | Kaolin from Lettin. | Kaolin from Kaschkau. | Kaolin from Sennewitz. | Paste of the Royal Porcelain Factory. |
|-------------------|--------------------|-----------------------|------------------------|-----------------------|---------------------|-----------------------|------------------------|---------------------------------------|
| | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. |
| Silicic Acid..... | 49.19 | 49.91 | 49.48 | 46.82 | 57.08 | 56.72 | 64.87 | 63.07 |
| Alumina.... | 36.73 | 35.99 | 36.64 | 38.49 | 29.94 | 31.07 | 23.83 | 24.67 |
| Iron Oxide.... | 0.81 | 0.63 | 0.66 | 1.09 | 0.65 | 0.59 | 0.83 | 0.59 |
| Magnesia..... | 0.18 | 0.30 | 0.40 | Trace | 0.49 | 0.22 | 0.50 | 0.40 |
| Potassium..... | 1.18 | 0.75 | 1.40 | 1.40 | 2.26 | 0.51 | 1.39 | 4.25 |
| Water | 12.41 | 12.34 | 11.99 | 12.86 | 9.87 | 11.18 | 8.36 | 7.00 |

TABLE B.

| | Kaolin from Ledez | Kaolin from Kottiken. | Kaolin from Tremosna. | Kaolin from Zettlitz. | Kaolin from Lettin. | Kaolin from Kaschkau. | Kaolin from Sennewitz. | Paste of the Royal Porcelain Factory |
|-------------------------------------|-------------------|-----------------------|-----------------------|-----------------------|---------------------|-----------------------|------------------------|--------------------------------------|
| | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. |
| Sum total of Mineral particles..... | 11.74 | 12.59 | 9.71 | 3.45 | 25.91 | 21.49 | 36.22 | 45.08 |
| In these particles | | | | | | | | |
| Silicic Acid..... | 9.05 | 10.65 | 7.91 | 3.04 | 23.28 | 21.29 | 35.98 | 38.09 |
| Alumina..... | 1.70 | 1.21 | 1.99 | 0.21 | 1.73 | 0.11 | 0.14 | 4.15 |
| Alkalies (as residue)..... | 0.99 | 0.73 | 0.71 | 0.20 | 0.90 | 0.09 | 0.10 | 2.84 |

finally the ordinary porcelain paste used in the royal porcelain factory at Charlottenburg, which is made from the kaolin of Sennewitz. When these different specimens were subjected to a chemical analysis their composition was found to be as shown in table A.

These figures do not give by any means a clear view of the nature of those kaolins and of the properties which one may expect from them in the process of manufacture. An essentially different view is presented when one tries to discover the composition of the real clay substance, i. e., of that product which results from the action of the weather upon feldspar and also the character of the non-weatherbeaten dust from constituents of the kaolins.

The separation of the component parts of the kaolins differing somewhat in their properties, was accomplished by means of a rational analysis, by decomposing the clays with concentrated sulphuric acid, as has been described more definitely in the preceding article. In this way we are able to separate the alumina, or clay substance from the mineral particles, and in these latter we determine the silicic acid they contain as well as the alumina, or it may be the sum total of both alumina and iron oxide. The quantity of non-weatherbeaten mineral particles contained in the kaolins mentioned, and their composition, are clearly shown in table B.

On the supposition already mentioned, that only quartz and feldspar are contained in this silicate residuum, it is practicable to estimate with the help of the chemical formula the quantity of feldspar in the alumina constituent. When the feldspar is deducted from that residuum the remainder gives the amount of quartz in the kaolin. So we get in percentages the amount of quartz, feldspar, and alumina contained in the kaolin. But the composition of the alumina can also be computed without difficulty with the aid of the elementary analysis given above and the ascertained amounts of silicic acid and alumina can be estimated in the silicate residuum.

Table C gives the percentages of the constituency of the kaolins in clay, quartz and feldspar on the one hand, and on the other hand, the composition of the alumina contained in them, as determined in the manner just described.

By this arrangement of the figures found by the general analysis, a clear insight is gained into the composition of the kaolins and the final result is obtained, as this table shows, that in all the varieties of kaolin the composition of the principal ingredient, which determines the character of the material as a whole, is nearly the same.

On looking more closely at the analyses given, we see at once that the differences in the various kinds of kaolin do not really

TABLE C.

| | Kaolin from Ledez. | Kaolin from Kottiken. | Kaolin from Tremosna. | Kaolin from Zettlitz. | Kaolin from Lettin. | Kaolin from Kaschkau. | Kaolin from Sennewitz. | Paste of the Royal Porcelain Factory. |
|---------------|--------------------|-----------------------|-----------------------|-----------------------|---------------------|-----------------------|------------------------|---------------------------------------|
| | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. | Per Cent. |
| Alumina | 88.26 | 87.41 | 90.27 | 96.55 | 74.09 | 78.51 | 63.77 | 54.92 |
| Quartz..... | 3.08 | 6.40 | 4.08 | 2.30 | 17.21 | 20.90 | 35.50 | 23.52 |
| Feldspar..... | 8.66 | 6.19 | 5.63 | 1.15 | 8.70 | .59 | .73 | 21.56 |

COMPOSITION OF THE ALUMINA IN THE KAOLINS EXAMINED.

| | | | | | | | | |
|----------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Silicic Acid.. | 45.36 | 44.76 | 45.98 | 45.36 | 45.63 | 45.00 | 45.30 | 45.46 |
| Alumina..... | 39.58 | 39.65 | 39.36 | 39.71 | 38.08 | 39.32 | 37.15 | 37.35 |
| Iron Oxide... | .92 | .72 | .73 | 1.13 | .88 | .75 | 1.29 | 1.07 |
| Magnesia.... | .20 | .34 | .45 | | .86 | .28 | .78 | .73 |
| Potassium... | .21 | .02 | .99 | 1.24 | 1.84 | .53 | 2.02 | 2.57 |
| Water | 14.02 | 14.07 | 13.28 | 13.32 | 13.32 | 14.20 | 13.11 | 12.74 |

lie in the composition of the alumina contained in them. This has, as we know, been determined heretofore by the researches of Forchhammer and Brogniart and Malaguti.

Now if, notwithstanding this agreement in the chemical constitution of the alumina, decided differences in properties are noticeable in the practical use of these kaolins, these must be attributed first of all to the kind and quantity of the undecomposed fragments of minerals contained in them. And in this respect there are (as is seen from the tables given) quite decided differences.

It becomes apparent, then, that in the kaolin clays which were examined (exclusive of the paste of the porcelain factory), there is a varying amount

of clay (alumina)... from 63.77 per cent to 96.55 per cent

of quartz from 2.30 per cent to 35.50 per cent

of feldspar from .59 per cent to 8.70 per cent

The variations in the proportional amounts of these substances

must cause essential differences in the behavior of these earths in the process of manufacture.

In the royal porcelain factory at Berlin the kaolin from Sennewitz is used for the ordinary porcelain paste. By taking this kaolin as a basis we shall get for practical purposes a definite composition of the paste which also meets the demands of technical purposes for its use in unbaked state as well as for its behavior in the kiln. In the same factory kaolin from Lettin is used for many purposes. If now someone should in an empirical manner simply substitute the kaolin of Lettin for the kaolin of Sennewitz in the porcelain paste in ordinary use, and in so doing count upon a similar behavior of the paste, he would certainly make a mistake, as can be easily seen from the result of the analysis.

Kaolin of Sennewitz. Kaolin of Lettin.

| | | |
|----------------|-------|-------|
| Alumina | 63.77 | 74.09 |
| Quartz | 35.50 | 17.21 |
| Feldspar | .73 | 8.70 |

In the royal porcelain factory, as we learn through the courtesy of Dr. Sarnon, the porcelain paste is composed of 200 parts of kaolin of Sennewitz and 60 parts of feldspar.

On the basis of our analysis of the kaolin of Sennewitz the composition of the porcelain paste can be computed:

| | |
|----------------|----------------|
| Alumina | 49.50 per cent |
| Quartz | 27.31 per cent |
| Feldspar | 23.64 per cent |

There was found

54.92 per cent alumina.

23.52 per cent quartz

21.56 per cent feldspar.

These insignificant deviations between the figures estimated and those actually found can probably be explained by the weighing on a large scale which is always somewhat inexact and by the variations in the hygroscopic water or perhaps also from the somewhat varying nature of the kaolin of Sennewitz, since the kaolin formerly used for the paste need not correspond exactly to the sample which we used recently in the investigation.

If now the kaolin of Lettin is substituted for the kaolin of Sennewitz in the paste, the composition of the paste would be expressed by the following analytical statement:

| | |
|----------------|----------------|
| Alumina | 56.99 per cent |
| Quartz | 13.24 per cent |
| Feldspar | 29.77 per cent |

It is clear that such a paste would be richer in clay and feldspar and considerably poorer in quartz. The result would be greater plasticity in molding doubtless, but greater shrinkage and increased fusibility in baking. This result obtained from the analysis agrees with the statements of Dr. Sarnon.

A discussion had recently arisen as to whether it was practicable to mix quartz with the porcelain paste. Herr Bunzli of Eichwald in a series of articles based on experiments and observations, has tried to prove not only the practicability but even the necessity of such an addition in moderate quantities for the Bohemian porcelain, which is manufactured from the kaolin of Zettlitz. Our analyses confirm his statements in a startling manner.

Herr Bunzli says that the kaolin of Zettlitz possesses decided plasticity and will therefore stand great compression, but that it exhibits great shrinkage and shows great activity in the fire. The figures which we have found for the kaolin of Zettlitz,

| | |
|----------------|----------------|
| Alumina | 96.56 per cent |
| Quartz | 2.30 per cent |
| Feldspar | 1.15 per cent |

give definite expression to these qualities. We can read out of them those qualities without ever having made practical experiments with the kaolin of Zettlitz. Bunzli adds that if feldspar is added to the kaolin of Zettlitz to the amount of only about 50-75 per cent spar-pastes would be obtained of moderate or great fusibility with dry biscuit surface and yellowish appearance; at the same time, however, there would be present objectionable spreading, warping and twisting. If, however, an amount of quartz is added identical with the amount of feldspar already in the paste, the paste would be much more quiet in the fire, less dry on its biscuit surface, of bluish-white color and greater translucency. The translucency and dense vitreous fracture characteristic of the real porcelain are not produced until the spar has acted upon the quartz and earth at a high temperature. Spar-pastes which are free from quartz produce a drier biscuit than those containing quartz. Bunzli proves the importance of the quartz in the spar-paste by direct experiments since he shows, among other things, that by rubbing quartz upon the surface of unfired porcelain figures biscuit figures are produced with a glaze like that produced in the welding flame or perhaps a semi-glaze. This phenomenon is caused by the fact that the feldspar shows basic properties in the welding fire and at this temperature exhibits a supersaturation with alkali.

If there is no quartz in the paste the alkali of the quartz acts upon the earth, the result in this case is no vitreous product, no glaze but an earthenware is produced; if, on the other hand, quartz is present, it attacks the alkali and the vitreous translucency, characteristic of porcelain, results. Bunzli corroborates these statements of his in part by direct experiments. If these results are accepted as correct, then the analysis of the kaolin of Zettlitz shows that the addition of quartz is evidently necessary since in its natural state it contains only 2.30 per cent of quartz while the kaolin of Sennewitz, for example, brings into the paste 35.50 per cent of quartz.

From these few remarks it will be seen how welcome and important a basis for the knowledge of kaolins and the composition of the pastes made from them is furnished by a rational analysis undertaken from the point of view of the manufacturing process. It affords a means of avoiding the uncertain empirical groping method, as well as a multitude of mistakes in practical experiments, and does away, likewise, with many obstacles in the manufacturing process which are occasioned by a variation in the raw material.

In closing, mention should be made, by way of suggestion, of one point which seems not to have been sufficiently explained; that is, the cause of the more or less decided yellow coloring of the spar-pastes. The variations in the iron percentage of the earths as determined by an analysis gives us no explanation of their phenomena.

The kaolin of Zettlitz shows the largest percentage of iron, e. g., 1.09 per cent, and yet it produces beautiful white porcelain. A hint is afforded by the remark of Bunzli that a spar-paste of this kaolin with 50-75 per cent of feldspar produces a yellowish biscuit, that, however, the same paste with the addition of the same amount of quartz as feldspar produces a biscuit of bluish-white appearance. It would be of value to hear the experience of our colleagues in this matter.

The Composition of Plastic Clays.

Our analysis of kaolins has shown that they consist of a mixture of three different chemically distinct materials, namely quartz powder, unweatherbeaten residue of feldspar or feldspathic rocks, and the real clay substance, i. e. hydrated silicate of alumina.

In this analysis of course only those kaolins could be taken into account which had been cleansed from all coarser admixtures, that is those in the refined state in which they are used in making pastes for finer claywares, especially porcelain.

The separation into three ingredients, one of which, the clay material, always uniform in its composition, forms by far the preponderating element, is generally practicable and is of importance since in making pastes the same materials have to be added by artificial means which appear in connection with the clay substance.

The variation in the properties of the kaolin is due to its constitution, i. e. to the greater or less proportion of quartz and feldspar, and it is therefore clear that when there is any variation of the kaolin in the production of pastes, allowance must be made for the amount of quartz and feldspar contained in it.

That which is true of the composition of kaolins can be assumed likewise in the case of other clays, but with this difference, that the latter, in consequence of the natural cleansing which is supposed to have invariably preceded the stratification, contain many other impurities so closely incorporated that their nature is difficult to determine.

Assuming then that there is a similar composition in the kaolins and plastic clays, there remains one question above all others to be answered: What difference exists in the clay substance, i. e. the hydrated silicate of alumina, which exhibits such different properties in the two materials and can the difference in its physical properties be explained from its chemical constitution?

The clay substance of the kaolins differs essentially in its qualities from that of the real plastic clays; the former is brittle and shrinks from a plastic dough to a loose friable mass; the latter dries up with great shrinkage to a dense hard hornlike brittle mass. These differences have an important influence upon the utility of the clay, and upon the manipulations necessary in working it up.

In answering this question only those clays were considered which could be compared to the kaolins in purity and freedom from accidental admixtures and since their use in the factory furnishes a valuable hint in this direction, only those clays were compared with each other which are used as raw material in the manufacture of pottery and stoneware.

The analyses which follow are partly those made for technical purposes in the chemical laboratory in the interests of the clay industry and partly those specially prepared for this investigation. The analyses apply to the following clays:

- I. Lean white stoneware clay of French origin, without definite statement as to the place where it was found.
- II. Fat clay of the same sort.

TABLE D.

| | I. | | II. | | III. | | IV. | | V. | | VI. | |
|-----------------------|--------|------------------------------|--------|------------------------------|--------|------------------------------|--------|------------------------------|--------|------------------------------|--------|------------------------------|
| | Total. | Insoluble in Sulphuric Acid. | Total. | Insoluble in Sulphuric Acid. | Total. | Insoluble in Sulphuric Acid. | Total. | Insoluble in Sulphuric Acid. | Total. | Insoluble in Sulphuric Acid. | Total. | Insoluble in Sulphuric Acid. |
| Sulphuric Acid..... | 75.35 | 54.87 | 60.49 | 27.76 | 62.16 | 30.73 | 65.89 | 38.52 | 63.11 | 31.91 | 56.14 | 20.17 |
| Alumina..... | 16.60 | .62 | 26.10 | .51 | 26.12 | .47 | 22.18 | .23 | 24.83 | .38 | 30.99 | 35 |
| Iron Oxide..... | 1.09 | | 2.11 | | .99 | | .71 | | 1.04 | | .80 | |
| Calcareous Earth..... | trace | | trace | | | | | | | | | |
| Magnesia..... | 0.53 | | .56 | | .39 | | .37 | | .32 | | .27 | |
| Potassium..... | 1.55 | | 1.08 | | .70 | | .48 | | 1.02 | | .78 | |
| Loss in Burning..... | 4.80 | | 9.80 | | 9.92 | | 10.27 | | 10.17 | | 11.27 | |
| | 99.92 | | 100.14 | | 100.28 | | 79.80 | | 100.49 | | 100.25 | |

TABLE D.—Continued.

| | VII. | | VIII. | | IX. | | X. | | XI. | | XII. | |
|-----------------------|--------|------------------------------|--------|------------------------------|--------|------------------------------|--------|------------------------------|--------|------------------------------|--------|------------------------------|
| | Total. | Insoluble in Sulphuric Acid. | Total. | Insoluble in Sulphuric Acid. | Total. | Insoluble in Sulphuric Acid. | Total. | Insoluble in Sulphuric Acid. | Total. | Insoluble in Sulphuric Acid. | Total. | Insoluble in Sulphuric Acid. |
| Silicic Acid | 60.76 | 27.56 | 59.28 | 22.98 | 78.22 | 59.35 | 64.53 | 33.14 | 70.12 | 44.19 | 54.28 | 21.44 |
| Alumina | 26.84 | 1.05 | 28.63 | 9.24 | 14.92 | .63 | 24.59 | .48 | 21.43 | .69 | 22.47 | .56 |
| Iron Oxide..... | .99 | | 1.29 | | .47 | | 1.01 | | .77 | | 11.42 | |
| Calcareous Earth..... | | | | | trace | | trace | | | | trace | |
| Magnesia | .52 | | .61 | | .35 | | .34 | | .39 | | 1.27 | |
| Potassium | 3.65 | | 3.44 | | 2.11 | | | | 2.62 | | 3.65 | |
| Loss in Burning..... | 7.26 | | 7.39 | | 3.78 | | | | 4.92 | | 7.05 | |
| | 100.02 | | 100.64 | | 100.15 | | 100.08 | | 100.25 | | 100.14 | |

III., IV., V., VI. Stoneware clays used in a large German stoneware manufactory, without statement as to their source.

VII. White clay from Eberhahn, near Coblenz.

VIII. White clay from Baumbach, near Coblenz.

IX. White clay from Bendorft, near Coblenz.

X. White clay from Lämmersbach, near Coblenz.

XI. White clay from Höhr, near Coblenz.

XII. Yellow clay burning red from Moschheim, near Coblenz.

The clays enumerated in VII.-XII. are those used chiefly in the Rhine pottery district.

The result of the chemical analysis is expressed in the table D. It should be stated that the alkalis were not distinguished but reckoned in every case as potassium. The decomposition of the alumina or its separation from quartz and fragments of feldspar was produced by heating in strong sulphuric acid.

The noticeable absence of potassium in almost all the clays examined leads us to conclude that we have to do here with the pure product of atmospheric action upon alumina rocks without any foreign admixtures worth mentioning.

In former analyses I have regarded the alumina contained in the part of the clay which is insoluble in sulphuric acid as belonging to the undecomposable residue of feldspar and have deducted from the silicic acid the part corresponding to the proportion of clay as silicate of feldspar (3.51 per cent silicic acid to 1 per cent of alumina) and have shown the reasons for this. If we do that in this case there remains as residue the percentage of quartz. When this computation is carried out the clays appear as a mixture of:

TABLE E.

| | I. | II. | III. | IV. | V. | VI. |
|------------------|-------|-------|-------|-------|-------|-------|
| Alumina..... | 44.63 | 71.54 | 68.82 | 61.48 | 67.80 | 79.47 |
| Quartz..... | 52.77 | 25.97 | 29.06 | 37.48 | 30.41 | 18.92 |
| Feldspar } | 2.60 | 2.47 | 2.12 | 1.04 | 1.89 | 1.61 |
| Residue | | | | | | |
| | VII. | VIII. | IX. | X. | XI. | XII. |
| Alumina..... | 71.22 | 76.30 | 39.71 | 66.23 | 54.73 | 78.07 |
| Quartz..... | 24.03 | 22.40 | 57.17 | 31.42 | 41.77 | 19.75 |
| Feldspar } | 4.75 | 1.30 | 3.14 | 2.35 | 3.50 | 2.18 |
| Residue | | | | | | |

Although this method of reckoning the analyses enables us to look upon the materials examined from a uniform standpoint, and to explain the differences in their properties by the variation in the

amount and degree of distribution of the quartz powder mixed with them, yet a much better idea of their peculiarities can be obtained by calculating from the analyses the composition of the alumina. This is done by deducting from the figures for the alumina the per cents of silicic acid, alumina and potassium corresponding to the per cents of quartz and feldspar in it and dividing the remainder into 100 parts. If this calculation is made the following figures show in per cents the composition of the clay substance (or really the part of the clay which cannot be dissolved in sulphuric acid).

TABLE F.

| | I. | II. | III. | IV. | V. | VI. |
|-----------------------|-------|-------|-------|-------|-------|-------|
| Silicic Acid..... | 45.99 | 45.75 | 45.67 | 44.27 | 46.16 | 46.52 |
| Alumina..... | 38.08 | 35.77 | 37.42 | 35.58 | 36.17 | 38.55 |
| Oxide of Iron..... | 2.44 | 2.94 | 1.44 | 1.15 | 1.55 | 1.01 |
| Calcareous Earth..... | trace | | | | | |
| Magnesia..... | 1.19 | .78 | .57 | .60 | .48 | .34 |
| Potassium..... | 2.36 | 1.24 | .39 | .45 | .97 | .56 |
| Loss in Burning.. | 10.76 | 13.70 | 14.41 | 16.67 | 15.93 | 14.32 |
| | VII. | VIII. | IX. | X. | XI. | XII. |
| Silicic Acid | 46.62 | 47.44 | 47.44 | 47.39 | 47.45 | 42.06 |
| Alumina..... | 36.01 | 37.21 | 35.74 | 36.40 | 37.88 | 28.06 |
| Oxide of Iron..... | 1.39 | 1.68 | 1.94 | 1.52 | 1.41 | 14.62 |
| Calcareous Earth..... | | trace | trace | | | trace |
| Magnesia..... | .73 | .79 | .88 | .51 | .71 | 1.62 |
| Potassium..... | 3.47 | 4.22 | 3.85 | 3.96 | 4.08 | 4.02 |
| Loss in Burning.. | 10.19 | 9.69 | 9.52 | 9.92 | 9.00 | 9.03 |

These figures show that all the clays contain only small quantities of undecomposed feldspathic mineral fragments, and that they appear essentially as a mixture of clay substance and quartz powder.

The most surprising thing about these figures is that they agree so nearly, which shows that the conjectures we made before are correct and that the clays which come in part from localities widely separated, have, nevertheless, almost the same constituency in alumina.

We find an exception only in the clay of Moschheim, which is very rich in iron, and this is easily explained. In this case we have to do apparently with a clay which the high per cent of iron oxide shows that it owes its origin, not to an alumina rock, but to minerals containing iron or those in which subsequently a deposit of iron hydroxide has taken place through the infiltration of waters containing iron.

In another respect, also, the figures show interesting results. The only essential differences between them are in the percentage of alkalis and water. On comparing the figures we find that the clay substances which have a large per cent of alkali show a less per cent of water, while those in which the percentage of alkali almost entirely disappears, show a decidedly larger percentage of water, so that it is a reasonable conclusion that they can replace each other. A higher percentage of alkali makes it appear that the clays possessing it are more easily compressed by slagging. The percentage of water produces greater porosity after burning, and thereby makes the slagging more difficult, which is reduced by the small percentage of alkali, and in fact the experiments in combustion which have been carried out show that the clays III.-VI., which are poor in alkali, are to be reckoned among the most highly refractory ones, while clays VII.-XV. possess only a low degree of refractoriness. It should be noticed further that the composition of the clay substance in clays VII.-XI., which are found in neighboring localities (the pottery district on the Rhine) show a surprising uniformity, so the differences in the composition of the clays are to be sought solely in the greater or less proportion of finely pulverized quartz.

Finally on comparing the composition of the clay substance of the plastic clays which have been examined with that of the kaolins, which was given in the preceding article, we find here, too, a remarkable agreement.

If from the analysis given in the preceding chapter we take the mean average of the composition of the clay substance of seven kaolins we shall get the following figures:

| | |
|-----------------------|-----------------|
| Silicic acid..... | 45.34 per cent. |
| Alumina | 38.98 per cent. |
| Iron oxide..... | .92 per cent. |
| Calcareous earth..... | |
| Magnesia | .52 per cent. |
| Potassium | .98 per cent. |
| Water | 13.62 per cent. |

These figures show such a great similarity to those given in the present article that except for the percentage of alkali, which is for the most part higher in the plastic clays, and which shows variations in the kaolins as well, we cannot discover any essential chemical difference. It is obvious then, that in the case of the purer plastic clays, as well as the kaolins, the difference in their behavior in the fire is due principally to the variations in the proportion of alkali and water in the clay substance.

No important facts, however, are given by the chemical composition with reference to the marked differences in the degree of plasticity, which is reduced to a minimum in the kaolins, even when there is higher percentage of pure waterproof silicate of alumina, a percentage which is usually very considerable.

The quality of plasticity seems, therefore, not to be peculiar to a certain chemical union, but in materials of like chemical composition to vary according to the degree of mechanical decomposition and the kind of molecular arrangement, and possibly the degree of plasticity is already determined in the structure of the rocks from which the clay originates.

The present investigations show most decidedly that it is not sufficient to know the composition of the clays as a whole in order to draw conclusions with reference to their qualities and to determine their utility for certain technical purposes, but it is necessary to go back to the difference in mineralogical constituent parts, and especially the composition of the element which predominates in quantity, the clay substance which in most cases gives character to the material.

Some Investigations with Regard to the Coloring of Bricks.

The clay substance in its purest form, kaolin, is white in appearance. All the phenomena of color which we observe in clays are due to impurities. Of these impurities iron, with its various compounds, is the most important. There is scarcely one of the raw materials used in the manufacture of pottery which is entirely free from iron. The compounds of iron are frequently present in very considerable quantities in the ordinary clays.

The only other substance occurring in combination with clay, which colors it and which must therefore be considered in this article, is manganese, and as this is never found except in connection with iron and always in very small quantities as compared with the latter, its power as a coloring agent is rarely effective.

The effectiveness of iron as a coloring agent depends not only upon the quantity in which it occurs, but also upon its degree of oxidation and upon a whole series of physical and chemical conditions of the clay, so that the shades of color which it produces are almost numberless. Therefore, when the more highly colored clays are employed in manufacture, great skill is necessary in the treatment of the raw material in order to obtain approximate uniformity of color in the finished products.

The compound of iron which plays the chief part in the coloring of pottery is ferric oxide. An examination of the gradations of

color which this exhibits in itself will explain the extraordinary variety of colors which it produces.

The shades of color assumed by chemically pure ferric oxide vary greatly according to the density of the oxide and the method of its production; thus the preparation made from ferric nitrate is brownish-red, that made from iron vitriol by gentle heating is red with a tinge of orange. In whatever way it is obtained the color of the ferric oxide always becomes darker when it is strongly heated and thus condensed, and the color deepens as the temperature is increased; at a strong white heat it passes into black-brown or dark violet. In general the coloring of clay products by ferric oxide will become darker in proportion as the temperature to which they are exposed in burning is increased. The color of the clay is also affected not only by the quantity and density of the ferric oxide present in it during the burning process, but also by the degree of porosity of the clay. It is a well known fact that colored bodies always appear darker in a dense mass than in a finely divided state, e. g., in pulverized form, that is, they are darker when little layers of air are embedded between the molecules as in the pores of clay which has not yet been burned to complete slagging.

The coloring is no doubt further influenced by the chemical condition of the ferric oxide present in the clay; that is, whether the iron is only mechanically mixed with clay or whether it has already formed compounds with the separate ingredients. In the latter case it exhibits different physical properties also and different colors. While ferric oxide in a free state always has a reddish or brownish shade, the glasses or slags, for example, which are colored by ferric oxide are colorless or yellow when a small per cent of oxide is present, yellowish brown or brown when the proportion is greater, and the shade of brown is one never seen in the free oxide.

We may assume that all the clays which consist of the real uncolored clay substance mixed with mineral particles or with mineral particles which have been seasoned by exposure to the air or with free ferric oxide or its hydrate, always receive after burning a shade of red or brown, the colors of the pure ferric oxide, which, however, are less pronounced in this case on account of the presence of uncolored clay substance. But we meet with entirely different color phenomena when substances are also present in the clay, which are capable of causing fundamental chemical as well as physical changes during the burning process.

We see this, for example, when carbonate of lime, which often occurs in considerable quantities in brick clays, is present. In

this case the red color produced by the ferric oxide at a lower temperature completely disappears again, under certain conditions, at the temperature at which slagging takes place, and does not re-appear except as the result of a defect in the smoking or firing process. Not only the lime and perhaps the magnesia, too, when the latter is present in considerable quantities, but also the clay constituent of the material seems to act in a similar manner, as will be explained further on in the discussion of the materials rich in argillaceous earth.

Besides the ferric oxide, that compound of iron which contains less oxygen must be considered, namely, the ferrous oxide; during the process of burning this is formed from the ferric oxide by the presence of carbonic substances in the clay or under the influence of the flame or if very high temperature, or it is sometimes present in the clay from the outset; on the whole, it has a much more powerful effect as a coloring agent than the ferric oxide.

It is a fact well known in glass works that iron in the form of ferrous oxide colors the glass pastes very dark green or black and that a decolorization or, if many impurities are present, a reduction of color takes place when the ferrous oxide is converted into ferric oxide by the addition of oxidizing substances such as manganese, saltpetre or arsenous acid. The coloring given to the clay by the ferrous oxide corresponds to the coloring of the glass and slags, i. e., it is green, violet or black according to the absolute amount of the iron and the relative proportions of these two oxides; in general, therefore, the formation of ferrous oxide is never desirable, at least in porous bricks, because of its deep color and its instability, and it is a normal ingredient only in the manufacture of densely slagged products, such as clinkers. If we wish to classify the clays according to the colors which they take on in the paste during the firing, without regarding the accidental or surface colors caused by defects in the process, we may divide them into four groups:

1. Clays containing much alumina and little iron. These burn white or with scarcely perceptible color.
2. Clays containing much alumina and a moderate proportion of iron. The color of these varies from pale yellow to leather brown.
3. Clays containing little alumina and much iron. The brick clays burning red.
4. Clays containing little alumina and much iron and lime. The yellow-burning brick-clays or clay-marls.

1. To the first group of clays belong the raw materials for the noblest products of the pottery industry, the kaolins, or porcelain

clays, and also a number of plastic clays. Since the products of the porcelain clays are often of pure white color, they are said to be altogether free from iron compounds, yet this statement is never entirely confirmed by chemical analyses. Bruno Kerl, in his well-known work,* gives a series of analyses of kaolins and porcelains, which show that the percentage of iron, which is very small in many cases, may exceed 1 per cent without having any appreciable effect upon the whiteness of the clay. A few instances may be given here. The proportion of ferric oxide in the porcelain of Nymphenburg was found to be 2.5 per cent, in the porcelain of Berlin .6-1.74 per cent, in the porcelain of Meissen .8 per cent, in that of China 1.2 per cent, in that of Limoges .7 per cent. This proportion of iron seems small in comparison with that of the ordinary clays. It is remarkable, nevertheless, that, although the porcelain was treated in the ordinary way, the colors vary so little that only a practised eye can detect any color at all.

The presence of large quantities of alumina (and in this instance we are concerned with the clays containing the greatest amount of alumina) will have upon the color of the ferric oxide an effect similar to that caused by the presence of large quantities of lime in the clay; a phenomenon which we shall discuss further indicates with reference to the color of the clays of the second group that a large proportion of alumina can under certain conditions entirely neutralize the color of the ferric oxide. Besides the porcelain clays a number of plastic clays should be put into this group which in burning take on a pure white color and are used in making clay pipes and fine faience.

2. The second group comprises the clays which in a gentle heat burn white occasionally with a tinge of pink, and at a higher temperature take on a more or less yellowish or brownish color, but which never show any shade of red and never turn green at a very high degree of heat. In this group are included the majority of the so-called plastic clays and also the refractory clays in all degrees of refractoriness down to the brown-coal clays, used at the present time only for bricks. These contain, as a rule, a comparatively high percentage of clay, 20 to 30 per cent and over, a percentage of iron, however, which in some cases approaches that in the brick earths, which burn red, but in most cases is considerably less (1 to 5 per cent).

These clays as well as those of the first group possess less interest for the brickmaker than the clays of the third and fourth group, just because they are often so highly refractory that they

*Bruno Kerl, *Abriß der Thonwaren Industrie*, pp. 434-441.

are not adapted to the manufacture of brick products; they are chiefly used in the nobler branches of the ceramic art and in the manufacture of firebricks. Only the least refractory of the clays belonging to these groups are used in making bricks and terra cotta wares, e. g., the yellow-burning, brown coal clays of Lusatia (the clays from Greppin, Siegersdorf and Bunzlau).

It seems that in these clays the high percentage of alumina destroys the red tint of the coloring iron oxide and changes it to a yellow or yellowish-brown, just as the lime does in other clays. The reason for this is not, as one might perhaps imagine, that in a mixture of red burning clays of the third group with white burning clays of the first group, the white material dilutes the red and produces pale red bricks, but the red actually passes into a yellow or brown. As an instance of such a mixture the familiar leather-brown bricks used as facing in the new bank building in Berlin might be mentioned.

A number of analyses of materials which belong to the class of clays just discussed, i. e., the clays with little lime which burn yellow or brown, afford an insight into the relation which the coloring iron oxide bears to the other ingredients without coloring properties, and gives us especially interesting data for comparing the different amounts of iron oxide with each other and with the similar figures which result from the analyses of red coloring clays given further on.

TABLE I.

| Clay from | Poole (England) per cent. | Senftenberg per cent. | Neuwied per cent. | Neuwied per cent. | Schönebeck per cent. |
|---|---------------------------------|--------------------------|-------------------------|----------------------|-------------------------|
| Silicic acid | 59.61 | 62.50 | 56.05 | 64.37 | 75.38 |
| Alumina | 26.81 | 21.30 | 25.05 | 21.91 | 15.01 |
| Ferric oxide | 2.03 | 3.06 | 4.68 | 3.04 | 2.39 |
| Calcareous earth | 0.82 | 0.58 | 0.97 | 0.70 | 0.80 |
| Magnesia | 0.44 | 0.53 | 1.23 | 1.37 | |
| Potassium | 2.77 | 2.18 | } 2.46 | } 2.99 | } 2.38 |
| Sodium | 0.80 | 0.81 | | | |
| Water and organic substances | 7.46 | 8.57 | 9.10 | 4.71 | 4.84 |
| Color after burning, (stock brick) | white or yellowish | bright yellow | yellow to leather color | yellowish brown | yellow |
| Proportion of ferric oxide and alumina... | 1:13.2 | 1:7.0 | 1:5.4 | 1:7.2 | 1:6.3 |

It is plain from the analysis that the absolute quantity of the coloring ingredient furnishes no reliable criterion for the color of the clay after burning; but the coloring is affected by a whole series of physical and chemical conditions which up to this time have escaped observation. All the clays mentioned have, however, this property in common; they all exhibit a shade of color varying from white or yellowish white to brown according to the temperature to which they were exposed.

In the color phenomena which they exhibit these clays show a similarity to the clays of the fourth group, those rich in iron and

TABLE II.

| Clay from | Rathenow* | Bockhorn** | Schwarzhutte, near Osterode, A. H.*** | Ottweiler. | Ulm. |
|--|-------------|--------------------------|---|-------------|-------------|
| Silicic acid..... | 61.30 | 70.22 | 79.43 | 68.34 | 56.33 |
| Alumina..... | 18.87 | 13.67 | 10.07 | 16.25 | 22.37 |
| Ferric oxide..... | 6.66 | 6.80 | 5.35 | 5.63 | 7.64 |
| Calcareous earth..... | 0.85 | | FeO.12 | | 1.46 |
| Magnesia..... | 1.20 | 1.30 | 1.40 | 1.49 | 1.86 |
| Potassium..... | } 3.20 | } 3.37 | 2.36 | } 3.79 | } 2.22 |
| Sodium..... | | | 1.62 | | |
| Water..... | 8.28 | 5.30 | | 4.32 | 8.10 |
| Color after burning, (stock brick)..... | dark red | dark red to violet | dark cherry red | dark red | dark red |
| Proportions: Ferric oxide: alumina..... | 1:2.8 | 1:2.0 | 1:1.9 | 1:2.9 | 1:2.9 |

*Washed.

**The material used in the manufacture of the Oldenburg street clinkers.

***Analysed after being burned.

lime, but are distinguished from the latter by their much greater refractoriness, since they are either classed outright with the fire-proof clays or at least resemble them closely, and since in the transition to the state of density required in porcelain, they never assume the green color characteristic of the calcareous clays, but usually have a brown or grey color.

It appears that in the representative clays of the second group cited above, the percentage of alumina is always greatly in excess of the percentage of iron oxide and that their ratio of weight varies in the examples given from 1 to 5.4 and from 1 to 13 and

upwards; from this we may infer with some show of reason that the clays of this group (presupposing equal temperature and approximately equal porosity) burn clearer, shading into white or yellow the less the amount of ferric oxide contained in them both absolute and relative as compared with the amount of alumina.

3. The third group embraces the clays which burn red. These are the most important and in general the most weather-proof materials used for bricks. They have a smaller percentage of alumina and for the most part a larger percentage of iron than the materials of the preceding group; they are, therefore, on the whole, more easily fusible. The amount of lime and magnesia as well as of alkalis, is, as a rule, very small in the most highly colored clays. The color in burning is at first a pale red; as the heat becomes more intense and the paste becomes more dense, the color changes to a dark red, then into violet red and finally into blue black.

The analyses in tables I and II of several brick clays which show the color phenomena characteristic of this group enable us to make a comparison between these clays and those described above.

It is evident that in these clays which in burning assume a decided red color, the relative proportion of ferric oxide and alumina is quite different from that of the preceding group, as the ferric oxide in this group equals only one-half or one-third the amount of alumina.

Although the analyses of the clays of the second and third groups show that the ingredients of these two groups differ only slightly in kind, and that there is little difference on the whole in the respective amounts of the ingredients used as fluxes, yet each group is distinctly characterized by the relative proportions of ferric oxide and alumina. Where the percentage of alumina is not more than three times the percentage of ferric oxide, the color is a decided red, but where the alumina exceeds the oxide by five and a half times or more, the color is distinctly brown or yellow; other factors are to be taken into account, to be sure, such as the degree of heat, the porosity or slagging of the clay, yet these factors do not essentially alter the division into groups, since they generally affect simply the shading of some one color.

Between the clays burning red and yellow there is a whole series of intermediate grades corresponding to a relative proportion of ferric oxide and alumina, in which the latter is sufficient in quantity to modify the red color, but not sufficient to produce a decided yellow coloring. Thus there arises a series of mixed colors and discolorations which are of no value in the manufacture

of facing bricks and terra-cotta products, since in these it is of primary importance to obtain a clear, decided shade of color.

4. The clays included in the fourth group are of equal importance with those of the preceding group. Here belong the materials rich in lime, which are often called clay marls. These demand the especial attention of the brickmaker because they are sensitive to coloring and more difficult to handle, owing to the fact that the differences in color become very marked in the process of burning.

TABLE III.

| CLAY FROM | VELTEN | *STET-TIN | NEUHOF NEAR STRAL- SUND | SZEGE- DIN* | BIRK- ENWER- DER | **LABY- SZYN |
|---|--|-----------|----------------------------------|----------------|------------------------|-----------------|
| Silicic Acid ... | 47.86 | 55.79 | 55.02 | 56.07 | 48.34 | 46.67 |
| Alumina..... | 11.90 | 9.29 | 13.90 | 14.02 | 11.63 | 3.06 |
| Ferric Oxid... | 5.18 | 5.79 | 4.53 | 5.49 | 4.59 | 5.31 |
| Calcareous | | | | | | |
| Earth... | 14.96 | 18.78 | 10.95 | 16.53 | 15.87 | 11.46 |
| Magnesia..... | 1.71 | 2.10 | 1.76 | 0.69 | 1.79 | 4.08 |
| Potassium..... | 2.65 | | 1.48 | | 2.78 | 3.33 |
| Sodium..... | 1.01 | | | | | 0.70 |
| Carbonic Acid | 10.44 | | 8.64 | | 11.71 | 10.40 |
| Water and Or- ganic Matter | 4.64 | | 3.31 | | 5.28 | 4.30 |
| Color after Burning.. | When partly burned red or flesh color, as stock-brick yellowish-white or sulphur-yellow, as clinkers yellowish-green or green. | | | | | |
| Proportion of Iron Oxid, Alumina.. | 1:2.3 | 1:1.6 | 1:3.1 | 1:2.5 | 1:2.5 | 1:2.4 |
| Proportion of Iron Oxid, Calcareous Earth... | 1:2.9 | 1:3.2 | 1:2.2 | 1:3.0 | 1:3.5 | 1:2.2 |

*After being burnt.

**According to the analysis of Dr. Michaelis after the iron sulphide which had been found was reduced to ferric oxid. Notizblatt, 1872, p. 155.

The clays containing a large proportion of lime present color phenomena which are in inverse ratio to those of the clays burning red and yellow. In the latter the color always becomes darker as the temperature is increased. In the clay marls the red color of the ferric oxide appears first at a low baking temperature; at a higher temperature, when the lime begins to exert a chemical action upon the silicates of the clay, the red color grows paler and passes through a flesh color into a white or yellowish white;

as the slagging proceeds the color becomes yellowish green or green, and finally, when the fusion is complete, dark green or black.

The coloring of these, as well as of all clays, is due to the presence of ferric oxide, but the red produced by the oxide is modified when lime is also present by the formation of yellow or white silicates of lime and iron; the conditions under which the formation of these silicates does not take place have been discussed in another article.*

The analyses in Table III show the composition of such calcareous brick materials burning yellow.

It will be seen from the figures given there that the absolute amount of water is approximately equal to that in the clays burning red, and it is also evident that the relative proportion of ferric oxide and alumina corresponds to that in the preceding group; as a matter of fact all these brick materials also yield red bricks, when partially burned; therefore it is often supposed that the proportion of iron is less in the yellow burning marls than in the red burning clays, because the bricks made from them frequently take on an almost white color; but this supposition is not at all justified, and it is not in accordance with the facts in the case of the above mentioned marls, which may be looked upon as types of such materials, although it is perhaps possible in certain instances, since the composition of the clays varies so greatly.

Professor Remele has emphasized the fact that the yellow color is due solely to the presence of considerable quantities of lime, which at the point when the slagging begins, forms a yellow or yellowish white compound with the other constituents of the clay; but it has not been determined what proportion must exist between the lime constituent and the other ingredients, especially the ferric oxide, in order to change the red color of the latter into yellow.

In the analyses given above the relative proportions of ferric oxide and lime vary in round numbers from 1:2 to 1:3, yet since the materials examined all show the characteristic yellow color, we may infer that the amount of lime might be diminished still more without destroying entirely the action of the lime upon the oxide.

An attempt has been made to solve this problem synthetically.

The clay from Rathenon, burning red, the analysis of which was given above, was mixed with pure calcium carbonate obtained by precipitation from calcium chloride in the proportion of 1, 2, 3...8 equivalents of carbonate of lime to one equivalent of ferric oxide. Reckoning in the small amount of lime contained in the clay, the relative proportion of ferric oxide and lime in the specimens appears as follows:

*Notizblatt, 1872, No. 4.

Specimen No. 0, 1:0.13; No. 1, 1:0.48; No. 2, 1:0.83; No. 3, 1:1.18; No. 4, 1:1.53; No. 5, 1:1.88; No. 6, 1:2.23; No. 7, 1:2.58; No. 8, 1:2.93.

These nine specimens in the shape of bars 10 cm. long and 1.5 cm. thick were placed together in a kiln heated by illuminating gas in a muffle surrounded by the flame, and were exposed first to a moderate red heat, so that they were all subjected to the influence of the heat under the same conditions; after cooling all the specimens were colored red, and no great variation in color could be observed. Then the specimens were exposed to a higher temperature, a bright red heat. After they were cooled again there was a difference in color; they were all in the condition known in brickyards as "stock brick." Specimens 0, 1, 2, 3, had remained red, but had taken on a discoloration in the paste in proportion to the amount of lime contained in them; No. 4 showed a yellowish brown crust about 1 mm. in thickness, but was still colored reddish in the center; in 5 and 6 the yellow crust was thicker; 7 and 8 showed on fracture a yellow color throughout, with a tinge of gray. From these phenomena it is evident that the yellow color appears first and most easily in the mixtures containing the greatest amount of lime, and it is also apparent that the relative proportion (1:2) of ferric oxide and lime (as in specimen 4) is sufficient to produce a yellow color, providing the heat is sufficiently intense and prolonged.

In all the analyses given above the amount of lime is in reality greater than that appearing in this proportion—it is even more than double the amount of oxide.

With the real yellow-burning clays are connected those in which the amount of lime is not sufficient to produce a yellow color; the latter however show a peculiarity which is always characteristic of the group of strongly calcareous clays, namely, the red color becomes paler as the heat is increased while in the red-burning clays it becomes darker under the same conditions.

In the preceding paragraphs only those color phenomena have been taken into consideration which are visible in brick materials in the paste and on the surface, so far as the color in these cases coincides with that of the fracture, and on the other hand only those phenomena have been considered which are apparently due to the action of the ferric oxide. Therefore in the analyses given above the iron was in every case given as ferric oxide.

Surface colorations which may be due to the efflorescence of saline compounds during the drying process, to the action of flame and steam during the firing, to the deposit of fine dust and alkaline vapors may, for the present, be left out of the account, since

they are either accidental or due to some imperfection in the manufacturing process. So there remain to be considered only the phenomena caused by the action of the lower oxide of iron, the ferrous oxide. The opinion is current not only among brick-makers but also among chemists that the red color of burned clays is due to the presence of ferric oxide and the yellow to ferrous oxide that therefore red bricks are produced in the parts of the kiln where the air has free access or when in the cooling process the air can strike the heated bricks.

Prof. Remele in an earlier work* has shown that in two varieties of brick clay examined in the academy at Berg,† both of which in the raw state show considerable quantities of ferrous oxide, one burning red and the other yellow, iron was present after burning in both in the form of ferric oxide only. From this fact he draws the conclusion that ferrous oxide is not a normal ingredient of porous burned clay products at all, but that it always changes into ferric oxide on being heated and that the yellow coloring in one case is due solely to the presence of a large amount of lime.

In the last general meeting of the German Association for the manufacture of bricks, etc. Herr Mendheim‡ stated that when bricks are burned with gas fire the yellow bricks burn red in the parts of the kiln where an oxidizing flame is present but remain yellow in a neutral or reducing flame. This statement induced me to take up the subject again. I examined a number of red and yellow bricks, those containing lime as well as those free from it (groups 4 and 2), with reference to the amount of ferrous oxide in them.

The test for ferrous oxide with ferric oxide, which formerly presented some difficulties in the case of a silicate insoluble in acids, was performed according to a modification of the Finkner method which was also made use of by Prof. Remele in his work, "Remarks Upon the Oxides of Iron in Clays and Upon Certain Reactions in the Brick-kilns." The modification consists in the use of finely pulverized native cryolite (fluoride of aluminum and sodium) free from iron in place of the calcium fluoride. The experiment is as follows: About 1 gr. of the material powdered as fine as possible and 2 gr. of cryolite were covered with 25 acm. of diluted sulphuric acid in a large platinum dish and boiled for some time. The completion of the decomposition of the silicate is indicated when the liquid which was dark colored at first becomes quite colorless and

*Remarks upon the oxides of iron in clays and upon certain reactions in kilns, *Notizblatt*, 1867, p. 119.

†*Notizblatt*, 1867, p. 119.

‡*Notizblatt*, 1873, p. 59.

almost clear, only slightly colored by some precipitated silicic acid or calcium sulphate. This takes place after boiling 15 to 20 minutes. Then it was diluted with half a litre of water (having been cooled externally) and the amount of ferrous oxide set free was determined by a solution of hypermanganate of potassium, the titre of which is known; the test for the total quantity of iron was made in the usual way by reduction in a sulphuric solution by means of amalgamized zinc and platinum and filtration with hypermanganate of potassium. From the total amount of ferric oxide and the difference of the oxide corresponding to the ferrous oxide the amount of ferric oxide can be computed. To avoid mistakes which might occur through impurities in the cryolite or the sulphuric acid employed a check experiment was made by dissolving 2 gr. cryolite alone in 25 acm. of dilute sulphuric acid and boiling; then diluting with half a litre of water and testing by a permanganate solution. A red color which showed the absence of reducing materials appeared after the first drop of the permanganate solution.

My work confirmed the results obtained by Prof. Remele and may be summed up as follows: I found ferrous oxide in all cases but in such small quantities that it could not possibly have any marked effect upon the coloring. I found also that the amount of ferrous oxide in porous bricks may be very considerable without causing noticeable differences in color while in clay that has been slagged like porcelain, i. e., in clay that is not porous, the variations in color are very marked.

Among the tests made for ferrous oxide especial emphasis should be laid upon those in which different colors of the clay are seen in the same brick, in which case we may conclude that the difference in color is not due to important chemical differences.

I will classify the experiments with ferrous oxide as I did the colors produced by ferric oxide and will then deduce the conclusions which may be drawn.

Brick clays contain in most cases a greater or less amount of organic substance which is destroyed in heating and in many cases causes a reduction of the ferric oxide. Thus the clay of Rathenow, when gently heated in a covered crucible, contains 2.20 per cent of ferrous oxide. But the ferrous oxide which has been formed seems unstable when under the influence of air admitted during the heating, and it is converted into ferric oxide. in the experiment with the clay of Rathenow mentioned above only .76 per cent of ferrous oxide appeared after heating about an hour under the admission of air, and the very small percentage of ferrous oxide noticed in all cases in bricks burned in the

normal way, from 1 to 3 per cent, may be considered as a residue which has escaped oxidation.

Group I. White clays, nothing.

Group II. Clays rich in alumina, poor in lime; burning yellow or brown:

| | Ferric oxide. | Ferrous Oxide. |
|---|----------------|----------------|
| Bricks from Senftenberg, yellow..... | 3.28 per cent. | .14 per cent. |
| Bricks from Senftenberg, whitish yellow | 3.29 | .42 |
| Group III. Clays burning red: | | |
| Building bricks from Rathenow..... | 7.07 | .18 |
| Clinkers from Schwarzhutte near Osterode, dark, cherry red..... | 5.35 | .12 |
| Ditto, greenish, gray..... | 3.43 | 1.85 |
| Ditto, blackish, violet | 2.14 | 3.01 |
| Group IV. Clays very rich in lime, burning yellow or green: | | |
| Yellow facing stones from Birkenwerder | 5.26 | .16 |
| Yellow Dutch stove tiles from Velten..... | 4.84 | 1.17 |
| Bricks from Neuhoof, near Stalsund, whitish red | 3.14 | 1.19 |
| Ditto, yellowish green..... | 2.01 | 2.85 |

| | Ferric oxide. P. C. | Ferrous oxide. P. C. | Sulphuric acid. P. C. |
|--|------------------------|-------------------------|--------------------------|
| Bricks of Hungarian shape, origin unknown, flesh red, and yellowish green: | | | |
| Red part | | .33 | |
| Yellow part | | .32 | |
| Bricks from Custrinchen, pale red and dark yellow: | | | |
| Red part | | .14 | 2.49 |
| Yellow part | | .15 | .11 |
| Stove tiles from Stettin, dark red and light yellow: | | | |
| Red part | 4.90 | .29 | 14.71 |
| Yellow part | 5.50 | .27 | .52 |

Pottery which contains a large amount of ferrous oxide produced by the so-called steaming which is customary in the Netherlands and also in England* has a blue-black or graphite-gray

*This practice is now universal.—Editor.

color, which can be produced by heating pieces of bricks of any color in a stream of hydrogen gas. But in every instance this dark color is very unstable in the heat. Steamed bricks take on their original color again if air is admitted through cracks in the kiln while they are cooling, and it is extremely difficult to preserve the gray or black color and is even quite impossible unless especial precaution is taken.

From this fact and from the preceding analytical proofs it is evident that the yellow coloring of the clay is in no case due to a constituent of ferrous oxide, and also that a red coloration of yellow bricks after or during the burning has no connection with the oxidation of the iron, since iron is also present as oxide in the yellow colored bricks.

I have shown elsewhere† that a red color can be produced in calcareous clays when the lime absorbs sulphuric acid from the oxygen of the flame, and since the calcium sulphate which is formed is only decomposed by the silicic acid at a heat above the baking temperature, the lime does not act upon the ferric oxide and the full force of the latter as a coloring agent is seen. In the two clay-pastes last enumerated, the yellow and red pastes, the cause of the coloring is likewise due to this according to the sulphuric acid tests.

But there is a second reason for the red coloring of the calcareous clays, and that is the circumstance that the temperature in burning was not high enough to cause complete action of the lime. I believe that the phenomena observed by Herr Mendheim are due to this alone.

It is a well-known fact that very high temperatures such as those used in the metallurgical treatment of iron and in the manufacture of porcelain, can only be obtained when there is an excess of combustible gases in the flame; i. e., when an intensive flame is used, as they say, and in a kiln in which the flame is oxidizing in one part and reducing in another, the temperature is always lowest where an excess of air is present, since in both cases the action takes place for the same length of time. So in the case mentioned above the reason for the red coloring is not due to the oxidizing effect of an excess of air, but to the circumstance that the temperature has been lowered by it. Even if under the influence of reducing oxygen gases ferrous oxide has been formed during the burning process, the burned products are under the influence of a stream of heated atmospheric air—especially

†Notizblatt, 1872, No. 4.

in a continuous kiln—at a high temperature long enough to allow a partial or complete return to ferric oxide.

This is proven by the following experiment. A bar of clay from Senftenberg about 1 cm. in thickness and about 8 cm. in length which had taken on a leather-yellow color when burned hard (percentage of ferric oxide 3.28, of ferrous oxide .14) was broken into two parts and one of them heated for some time in a stream of hydrogen to a moderate red-heat and allowed to cool in the stream of oxygen. When broken the clay showed a uniform ashy gray color in the fracture and on the surface. A gray piece was then heated about two hours in a platinum crucible and air was admitted. On cooling it was again colored yellow throughout and the shade coincided perfectly with the original shade.

But it is not alone in porous clays like the one used in this experiment that there is a re-oxidizing to ferric oxide on cooling; this also takes place in clays already slagged like porcelain, although in the latter case the return to ferric oxide is greatly retarded by the density of the paste. This is shown by an examination of a clinker from Schwarzhutte. The clinker in question had on the outside a deep pure cherry red color; the fracture showed that it was perfectly vitrified and entirely homogeneous. In the center of the brick there was a red core coinciding in color with the surface surrounded by a dark colored zone about 2 cm. wide. The transitions in color were alike on both sides, and showed the following gradations from the center outwards: cherry red, grayish red, grayish green, blackish violet, gray green, grayish red, cherry red. The outer red color, the real brick color, appeared in a stratum which was in most places not more than 1 millimeter deep; the grayish red layer was likewise very shallow and did not furnish sufficient material for analysis, but the cherry red, the grayish green and the violet strata were examined.

The dark color deepens in proportion as the percentage of ferric oxide is increased. This phenomenon can only be explained in this way: Beginning at the surface there is a reduction from ferric oxide to ferrous oxide under the influence of the flame, yet this action has not advanced to the center. Later on when cooling takes place, oxidation beginning also at the surface, takes place, which has caused at the surface a complete restoration to the original color of the brick and—at least in the deeper-lying strata—has caused a decrease of the percentage of ferrous oxide without reaching to the parts in the interior of the paste which are most reduced.

The analysis resulted as follows:

| | Cherry red | Gray green | Blackish-violet |
|--------------------|------------|------------|-----------------|
| | part. | part. | part. |
| | P. C. | P. C. | P. C. |
| Silicic acid..... | 79.43 | | |
| Alumina | 10.07 | | |
| Ferric oxide | 5.35 | 3.43 | 2.14 |
| Ferrous oxide..... | .12 | 1.85 | 3.01 |
| Lime | Trace | | |
| Magnesia | 1.40 | | |
| Potassium | 2.36 | | |
| Sodium | 1.62 | | |
| | <hr/> | | |
| | 100.35 | | |

The Influence of Furnace Gases Upon Clay and the Accompanying Color Phenomena.

The variations in color, which are not exhibited in clay in its native state, but which are produced in unglazed pottery by the firing process, are due to two causes.

1. A more or less vigorous chemical action, which may be caused by a mere increase of temperature, or by the action of the substances contained in the furnace gas.

2. A more or less thorough condensation of the paste by means of slagging, that is, a physical change.

A careful study of these causes and an investigation of the details of the firing-process will enable us to decide to what the uneven coloring is due, which is so frequently observed especially in the operation of the annular kiln, and the investigations presented below will throw more light not only upon the colorations produced in the annular kiln, but also upon those exhibited in other kilns.

In view of the variety of substances present in the furnace gases and the variable behavior of the clay towards them, taking into account also the complexity of the phenomena, it seemed necessary, in order to determine the chemical influences exerted upon the pottery wares during the firing process, to adopt the synthetic method, that is, to produce artificially the colorations, and to note the chemical changes connected with these phenomena.

In this way each change in color can be traced back to the action of a single substance or of several substances present simultaneously. We shall see also in the further course of our observations

that the results obtained by this method are not only very interesting and capable of direct application in the practical management of the kiln, but that they also throw light upon nearly all actually occurring color phenomena and are therefore calculated to arouse the greatest interest.

The constituents of the furnace gas, whose action upon clay was studied may be classified as normal and accidental. The former are those present in every form of combustion, no matter what material is consumed, and have of themselves, an oxydizing or reducing effect. The latter owe their presence in the furnace gas to impurities in the material employed.

The substances which may be regarded as the normal constituents of the flame are: Nitrogen, oxygen, carbon dioxide, carbon monoxide, hydrogen, ammonia, hydro-carbons and steam. The accidental constituents, which are nearly always present in furnace gases are: Sulphur vapor, and sulphuretted hydrogen, carbon bisulphide, and sulphur dioxide. Some of these substances were left out of the account, since they have no effect upon the action, even at a high temperature; these were nitrogen and carbon-dioxide, and also steam; since the detrimental influence of this latter substance is felt only at the low temperature at which it becomes condensed and is absorbed into the pores of the unburned clay.

These substances were obtained separately in as pure a state as possible. It is not necessary to give here the details of their production. I shall merely state briefly what clays were examined and in what manner the action upon them was brought about.

In the present essay I have divided the clays into four classes according to the colorations which they exhibit in burning, and, as will be seen below, I investigated a specimen of each class.

1. Yellow burning, ferruginous, calcareous clays—clay marls. Specimen examined—brick clay from Birkenwerder.

2. Red burning clays, poor in alumina, ferruginous, non-calcareous—the red burning brick clays and loams. Specimen—meadow clay from Rathenow.

3. White or yellow burning clays, ferruginous, and non-calcareous—pipe clays; plastic, refractory clays; brown-coal clays. Specimen—clay from Greppin near Bitterfeld.

4. White burning clays, poor in iron and rich in alumina—kaolin. Specimen—kaolin from Zettlitz.

Small quadrangular plates from 4 to 5 mm. thick were made from these four clays and a number of these were placed in a large covered platinum crucible with a perforated porcelain cover. Then a vigorous stream of the gas which was to be studied was

conducted through a small porcelain tube into the crucible, while the latter was brought to a bright red heat over a three-rayed gas jet.

Color phenomena of the yellow-burning calcareous clays (clay from Birkenwerder).

The action of oxygen alone introduced thus into the experimental crucible resulted in the production, after heating, of the following colors:

At a dark red-heat, dingy-red; at a moderate red-heat, flesh color; at a strong red-heat, yellow, shading into brown.

The chemical change in the clay connected with these colorations consists in the expulsion of the water and carbon dioxide, the combustion of the organic material, the oxydation of the iron compounds to iron oxide, and the uniting of the iron oxide and lime with silicates of the clay into a light colored compound.

For all practical manufacturing purposes we can draw from this experiment the following conclusion: In the presence of a preponderance of unconsumed oxygen in the furnace gas, the calcareous clays assume a color which varies, according to the temperature, from dingy red to light yellowish brown.

The action of hydrogen. Even when the action of pure hydrogen was of short duration and when care was taken to cool the specimens under exclusion of air, which was accomplished by the introduction of the hydrogen until they were completely cooled, the result was a deep uniform blackening of the paste appearing both on the surface and in the center.

Let this blackening disappear again after the clay is heated again a short time under the admission of air, that is, in the presence of oxygen; the colors then reappear which are produced when the heating takes place in an atmosphere containing oxygen, but with this difference, that at a moderate red-heat the flesh color shades more into whitish red and at a bright red-heat the yellow shades into yellowish green.

Since this blackening appears even when the specimens have previously been thoroughly heated and when pure hydrogen is used, it cannot be due to carbon, but is caused by the reduction of the iron compounds first to black magnetic oxide of iron and ferrous oxide and finally to metallic iron, as will be shown later. When the clay is heated with admission of air, this blackening disappears again, and when the heating in the air has continued for two hours no ferrous oxide, but only ferric oxide is present in the clay. From this it appears that even the bright colors of

calcareous clay are always due to the final oxidizing action of the air during the burning or cooling process.

The other reducing substances present in the furnace gases, carbon-dioxide, hydro-carbons and ammonia produce the same colorations as hydrogen.

The effect of the reducing gases can therefore be summed up as follows: They all produce a blackening which, when air is admitted, passes again into the colors which are characteristic when the heating takes place under admission of air. However, after a previous reduction the colors which appear again under the action of oxygen are lighter than without such reduction, i. e. they shade off into whitish or light green colors.

A temporary reducing flame in the kiln aids essentially in developing the bright flame of the calcareous clays.

The phenomena caused by the presence of sulphur compounds in the furnace gases were of especial interest, after I had previously demonstrated that the deep red flames and spots formed during the burning—especially in the annular kilns—were due to the absorption of sulphuric acid, which is frequently very marked.

A specimen of the clay of Birkenwerder, heated for two hours at a dark red-heat in a mixture of sulphurous acid and air, showed a dark reddish brown color and contained 13.60 per cent of sulphuric acid.

The same clay heated in a stream of illuminating gas which was fed at the same time with carbon bi-sulphide, assumed a leather brown color, had a strong odor of sulphuretted hydrogen when breathed upon, and contained sulphur to the amount of 6.75 per cent. When the clay was heated in the air, the leather brown color disappeared, sulphurous acid being formed in the meantime, and passed into the same deep reddish brown color which appeared when the heating took place in the mixture of sulphurous acid and air. After this re-oxidation the amount of sulphuric acid was 14.11 per cent.

When the clay was heated in an atmosphere of sulphur vapors, or sulphuretted hydrogen, or in mixtures of hydrogen, carbon-dioxide or illuminating gas with sulphurous acid, the same phenomena appeared as in the case of carbon bi-sulphide.

All kinds of sulphur compounds in the furnace gas are, when oxygen is present, or when it is absent and other combustible gases are present in place of it; seized upon with great avidity by the calcareous clays and calcium sulphate, calcium sulphide and iron sulphide are formed; when oxygen is admitted the last two likewise form calcium sulphate.

In connection with this reaction a deep red coloration appears which begins at the surface and grows paler toward the center.

But the clay which is colored red by the absorption of sulphur compounds loses this color entirely when it is kept for a time in a reducing atmosphere, free from sulphur, since in this case the sulphuric acid is decomposed again by the reducing influences into volatile sulphurous acid and the lime is taken up into the silicate. This reaction, which is exactly the opposite of the preceding one, takes place, however, only at a high temperature, not at a moderate red-heat.

In one specimen the sulphur, which amounted originally to 14.11 per cent, was reduced to 2.31 per cent after the clay was heated half an hour in a stream of illuminating gas, and afterwards in the air, while the dark red color had passed into a yellowish green.

In the presence of oxygen, and also in the presence of reducing gases, (carbon dioxide, hydro-carbons, hydrogen, etc.) sulphur compounds are taken up in considerable quantities by the lime and iron constituents of the clay marls at a low or moderate red-heat, and this absorption is always indicating by a very deep red coloring of the clay.

At a high temperature this deep red color caused by the absorption of sulphuric acid is entirely removed again by the action of reducing gases (hydrogen, hydro-carbons, carbon dioxide) and reverts to the normal yellowish-green color.

Color phenomena of the red-burning, ferruginous, non-calcareous clays—clay from Rathenow.

In the clays of this class, which are used very frequently in the manufacture of pottery and terra-cotta wares, the colorations caused by the action of the constituents of the furnace-gas are much less strongly marked than in those of the preceding class, and therefore manufacturers experience much less difficulty in producing pure colors. The different shades of color are in this case caused chiefly by the greater or less proportion of iron oxide and by the degree of condensation acquired by the clay during the burning.

In the experiments with this clay the action of the air alone during the beating caused the characteristic red color of the clay to appear, and this red color is deeper in proportion as the temperature is increased.

The chemical change in the clay consists in the expulsion of the chemically combined water, the combustion of the organic

matter, and the conversion of all the iron compounds to ferric oxide.

Under the action of hydrogen and of the other above mentioned constituents of the furnace-gas which likewise have a reducing effect (carbon dioxide, hydro-carbons, ammonia,) the same colorations which we observed in the clay of Birkenwerder appear in the clay of Rathenow, but with a deeper shade, since the proportion of iron is greater in the latter case. When the specimens of the clay of Rathenow were heated in a reducing atmosphere and subjected to the action of pure hydrogen, the color was grayish-black when the action lasted a short time, and velvety-black when it lasted longer. Since this kind of clay contains a large amount of iron, the action of the hydrogen could be studied better than in the others, for the hydrogen can act only upon the iron compounds, since only these can be affected by reducing or oxidizing influences at the temperature used in burning.

Several tablets of the clay of Rathenow, weighing together about 10g. were heated strongly in a stream of air for several hours until after repeated weighings they showed no more loss of weight. A tablet was then taken out and it appeared on examination of this that all the iron compounds had been converted into the red-coloring ferric oxide. The proportion of ferric oxide was 7.27 per cent. The specimens were heated again in an atmosphere of pure hydrogen. A loss of weight was now apparent since the ferric oxide, by giving up its oxygen was converted into a lower stage of oxidation.

From this loss of weight the extent of the action of the hydrogen, or of the other elements of the flame which act in a similar manner, may be found by calculation. The details of this calculation cannot be given here. It will answer our purpose to give the results.

The clay of Rathenow, after being heated two hours at a cherry-red heat in a hydrogen atmosphere, contained 1.97 per cent of ferric oxide and 4.77 per cent of ferrous oxide; after being heated two hours more at a bright red heat it contained .88 per cent of ferric oxide and 5.53 per cent of ferrous oxide; and after the heating was continued another two hours at a still higher temperature, it contained .00 per cent of ferric oxide, 6.01 per cent of ferrous oxide, and 0.21 per cent of metallic iron. In every case the color was black and became deeper as the temperature was increased.

From this it appears, (and the colorations of calcareous clay show the same result) that the color produced in the clay by the

ferrous oxide, which is formed by the action of reducing influences, is black and not white as has often been assumed heretofore. But it is also clear that when these influences act for a long time the final effect may be the separation of the metallic iron and this takes place sooner perhaps in the case of carbon dioxide and hydro-carbons.

The black color produced in strongly ferruginous clays by reducing influences, a color which is intentionally obtained in the so-called "blue steaming" process, is very unstable, as we have seen from the foregoing experiments and the process is reversed when oxygen is admitted in the glowing heat. After the clay is heated a short time with admission of air, the usual red color appears again owing to the conversion of the iron compounds into ferric oxide, yet the color is not as bright as that which appeared before when the heating was accomplished with admission of air.

Hence we find that reducing influences which appear temporarily in the kiln are not favorable to the production of the pure brick-red color, which is most desired. In the case of calcareous clays the contrary was true, as we have seen.

The effect of the compounds containing sulphur was likewise shown to be essentially different from that in the case of the calcareous clays already mentioned.

Sulphurous acid in the oxidizing flame, the action of which is exhibited in these experiments when the clay is heated in a mixture of sulphurous acid and air, produced neither a chemical change nor a change of color in the clay.

On the other hand when reducing gases are present in the flame, sulphur compounds are absorbed by the clay and iron sulphide is formed simultaneously with the appearance of the black color. The clay from Rathenow, after being heated a short time in a flame of illuminating gas fed with carbon bi-sulphide, was found to contain 2.99 per cent of sulphur. But when the clay is heated in the air this sulphur is entirely consumed again, and the red color, shading into violet, returns and is even more vivid than before. Quite like carbon bi-sulphide in their behavior are hydrogen sulphide, or mixtures of sulphurous acid with hydrogen, carbon dioxide or hydro-carbons.

Therefore with clays strongly ferruginous but non-calcareous the presence of sulphur compounds in the flame of the kiln is without effect when there is an excess of air in the gases of the flame, but in the presence of reducing influences is favorable to the production of a bright red color.

Colorations of the yellow-burning, non-ferruginous, non-calcareous clays—clay from Greppin near Bitterfeld.

These clays are characterized by the fact that they, when heated in the presence of air, assume at a low temperature a pale red or yellowish red color—flesh color—which at a higher temperature becomes yellowish-white and at a bright red-heat passes into sulphur-yellow or straw color.

Under the influence of reducing gases in the flame, the color assumes a blackish tinge as in the other clays. The clay of Greppin when subjected to the action of pure hydrogen had a clear ashy gray color after being heated at a dark red-heat and contained 1.69 per cent of ferric oxide and 1.01 per cent of ferrous oxide; after being heated longer at a bright red-heat it was dark ashy gray and contained 1.81 per cent of ferrous oxide and .34 per cent of metallic iron.

It is evident from this that the presence of ferrous oxide produces a dark color which has nothing in common with the real colors of the clay.

Even this gray color disappears again very quickly when air is admitted, but the original colors do not return, as they do when the clay is heated in the air, but the colors which do appear are noticeably paler; the flesh color which is distinctive for the lower temperatures is changed to whitish-yellow while at a higher temperature a pure yellow appears.

Consequently a temporary reducing atmosphere in the furnace must aid in the production of the desired yellow color in these clays too, as we have seen that it does in the clays of the first class.

Sulphur compounds do not, in the presence of air, cause any chemical action in the clays of this class and do not cause any change of color. The clay, when heated in a mixture of sulphurous acid and air, does not absorb any of the sulphur compounds and it has the same color as in the air alone. But sulphur compounds, in the presence of reducing gases, are absorbed readily by these clays, as by those discussed above, and a gray coloration appears such as we have observed in every instance when reducing gases are in action.

The clay of Greppin, after being heated two hours in an atmosphere of illuminating gas and carbon bi-sulphide, emitted a strong odor of hydrogen sulphide, when breathed upon, had a dark ashy gray color and contained 2.77 per cent of sulphur. Yet this sulphur and the gray color also disappear entirely when the clay is heated a short time in the air, but the yellowish color character-

istic of the action of the air upon these clays does not return; in place of it a red color appears, deepest at the surface, but extending through all the paste. This red color is deeper and has more of a violet-red tinge, the higher the temperature at which the action of the sulphuretted reducing gas took place. However this red color does not have the same intensity under all circumstances; it is deepest under the action of carbon bi-sulphide alone or of carbon dioxide containing carbon bi-sulphide, less deep when carbon dioxide or hydrogen is present in the sulphuretted atmosphere and cannot be produced at all by a mixture of hydrogen and hydrogen sulphide.

Even under the action of sulphuretted illuminating gas the red color could not always be produced artificially in the clay. From this it appears that the presence of large quantities of hydrogen or hydro-carbons retards or prevents altogether the appearance of this peculiar red color while the presence of much carbon dioxide together with the sulphur compound aids its appearance. This red color does not disappear when heated, even at a high temperature with admission of air, but if the color is not very deep, it does disappear under repeated alternate action of air and reducing gases free from sulphur (illuminating gas, hydrogen, etc.), and then the ordinary yellow coloring of the clay reappears.

If the color was a deep red it does not disappear again under the alternate action of reducing and oxidizing influences, but passes through a brownish-red into a leather-brown color.

The chemical process corresponding to these changes of color, which are so interesting and so important in manufacturing, is not easy to explain since no permanent chemical change took place in the clay with the red coloring and especially since an increase in the amount of ferric oxide cannot be assumed. If I do nevertheless attempt an explanation, it must be understood that such an explanation must be confirmed by further experimentation.

The iron constituent of the clay is found usually in chemical union with the other constituents and consequently produces only a pale yellow color, which is also the case in the calcareous clays. By a simple reduction of the ferric oxide to ferrous oxide, the iron remains in this union since the ferrous oxide possesses strongly basic properties and after the re-oxidation nothing is changed in the composition of the chemical compound. But if this reduction is accompanied by an adsorption of the sulphur, iron sulphide is formed which is not basic. The iron is released from

the chemical compound and is converted after its oxidation, into free coloring ferric oxide, which is only mechanically mixed with the clay paste.

Therefore the action of sulphur compounds in the non-calcareous clays may be summed up as follows: Sulphur compounds have no effect upon the clay in the oxidizing flame, in the reducing flame they produce a red color in the whole mass and the production of this color is aided by many carbon compounds in the furnace gases, and retarded by many hydrogen compounds.

Frequently repeated alternate action of oxidizing and reducing gases. In the absence of sulphur compounds causes this red color, if it is not very deep, to disappear at a low temperature and changes it to a leather color at a high temperature.

Colorations of the white-burning clays, rich in alumina and poor in iron—kaolin from Zettlitz.

These clays, which are used rarely if at all in the manufacture of bricks and terra-cotta wares, but which are of very great importance for the noblest products of the clay industry, since they furnish the pastes for porcelain and stoneware, act in all essential points like those just mentioned. At a high temperature, in the presence of oxygen, they assume a more or less pure white color, which is affected especially by the greater or less, proportion of iron, a proportion which is however always small.

Under the action of reducing gases they assume a dark color just as the other clays do, yet when hydrogen acts upon them this color is only a faint light-gray pervading the entire paste, since the amount of iron is small, a dark coloration appears only when the reducing gases contain carbon. Since these clays are for the most part highly refractory and consequently possess considerable porosity, when slightly burned, the gray color caused by the action of reducing gases quickly disappears when air is admitted and permits the pure white color to appear again (at least this is the case with the kaolin of Zettlitz).

The action of sulphurous acid, when oxygen is present at the same time, has no effect upon these clays and can cause no change of color, but, as in the other clays, it is the sulphur compounds in the presence of reducing gases which cause a marked coloration. Kaolin from Zettlitz, when heated two hours in an atmosphere of carbon bi-sulphide and illuminating gas, as in the earlier experiments, was shown to contain 1.12 per cent of sulphur. This sulphur disappeared completely when heated with admission of air, yet the color of the kaolin did not become white again, but

assumed a beautiful pinkish-red shade. Just as in the case of the yellow coloring, brown coal clays discussed above, this color, which pervades the whole mass, became deeper in proportion to the amount of carbon in the sulphuretted reducing gases and became paler in proportion as the hydrogen compounds were in preponderance in the gases; it could also be made to disappear entirely under the alternate oxidizing and reducing action of reducing gases free from sulphur.

The Action of Water in the Firing of Pottery.

Many phenomena which arise in the firing of pottery and which cause a considerable loss of material are attributed by the potter to the action of steam, but in most cases no satisfactory explanation of this action has as yet been found.

Experience has shown that the appearance of cracks or discolored filmy or floury coatings, and of variegated colors on the surface of the paste, the scaling off and tarnishing of its glaze, the disappearance of certain colors, etc., have some connection with the vapors which pass through the kiln, since they occur, or are more noticeable at least, when there is an increase in the amount of steam formed, which may be due to the putting in of wet wares, to repairs of the kiln or to moist fuel. Although such a connection exists without doubt, it has never been explained just how the steam, which is itself stable and indifferent towards complex silicates, can produce the above-mentioned phenomena. Upon some of these points at least light has been shed by experiments which will be described below.

Clay, or rather the paste prepared from clay, is highly hygroscopic, and when thoroughly dried it absorbs moisture from the air with great avidity and condenses it within its pores.

If thoroughly dried clay is put under a glass bell beside a dish filled with water, and is kept at a rather high temperature, perhaps in a chimney-flue, it will have a clammy feeling after a few days, and when both clay and water are weighed by means of delicate scales the latter will show a considerable loss in weight and the former a corresponding gain.

In general, the more unctuous the clay the more marked are these hygroscopic properties, and the water absorbed in a few days at an ordinary temperature often amounts to more than 10 per cent of the weight of the clay. The rapidity and energy with which this absorption of water takes place depends upon the amount of steam in the air which comes in contact with clay, and since the capacity of the air to absorb steam increases greatly as the temperature rises, the clay must absorb water more rapidly at a high temperature.

It is clear, therefore, that ware just put into the furnace in the first stages of the firing must absorb considerable water from the furnace gases and it is a well-known fact that under certain circumstances this absorption of water causes softening of the molds and even a more or less decided change in their shape.

The amount of moisture in the air surrounding the ware in the furnace depends upon circumstances which are in most cases accidental; e. g., the dryness of the pots, the strength of the draft, the condition of the furnace as regards dryness, the kind of fuel, etc.

Usually there is considerable moisture present, so that even at a rather high temperature the simple condensation of so large a quantity is sufficient to account for the detrimental effects produced.

This is illustrated by several experiments which were made under comparatively favorable circumstances, since in this case the water contained in the fuel may be regarded as the only source from which steam was derived. The object of the experiments was to determine the amount of steam present in the ordinary firing in the porcelain furnaces of the Royal Porcelain Factory. The results were as follows:

In the firing of a small, circular, two-storied trial furnace for porcelain, 1.0 m. in width and 1.75 m. in height, where the fuel used was dry wood on back-flame hearths, two tests showed that steam was present in the proportion of volume 17.88 and 15.37; in the firing of the gas furnace of the Porcelain Factory the proportion of volume was 9.72 and 7.75.*

The dew point of the furnace gas would therefore be fixed at 58.5 or 55.5 degrees C. in the first case, and at 46.5 or 42.0 degrees C. in the second case; i. e., the furnace gases are so charged with steam that when they are cooled below the temperature just given they would necessarily precipitate water in the form of vapors or sweat upon the surfaces of the pottery wares with which they come in contact, even if the clay did not possess hygroscopic properties.

Now, if such a precipitation of vapor in the pores or upon the surface of pottery wares is regarded as chemically pure water which must evaporate again at a higher temperature without leaving a residuum, the only phenomena which could be accounted for by this vapor would be those connected with the softening of the molds; but these precipitates do not consist of pure water, and the phenomena attributed to the water are not caused by the water itself, but by the substances which are present in connection with it.

The water is, however, indirectly the cause of the phenomena

*Illustrated and described in G. Möller's "Die neue Baumanlage der Königl. Porzellan Manufactur zu Berlin." Berlin, 1873. Pub. Ernst & Korn.

usually attributed to it, since by penetrating into the pores and condensing upon the surface it serves as a medium for the absorption of the injurious substances.

In order to determine the nature of the substances which are present in connection with the steam, and which must have their origin in the paste of the pottery wares or in the fuel or in the ashes of the fuel, an attempt was made to precipitate large quantities of moisture from the furnace gas in the above-mentioned kilns. Interesting results were obtained from an examination of these precipitates, for, to a certain extent, the least possible amount of impurities is represented here, since the fuel used in producing the flame was relatively the purest, wood and generator gas from pure lump coal; if the fuel had been less pure the steam would presumably have contained larger quantities of the impurities, a supposition which is confirmed by actual experience.

The condensable constituents of the furnace gas were obtained in the following manner: A long glazed porcelain tube was fitted into the door of a furnace in such a manner that it projected about 5 in. into the interior of the furnace. This was connected with a Liebig cooler, which was provided with a U-shaped condenser and the latter was brought into connection with a receiver by means of a pipe tube in the curve. Cooler and condenser were kept cool by water at 15-20 deg. C., and a stream of furnace gas was drawn through the whole apparatus during the entire time of the firing by means of a rubber bag provided with valves. A liquid, colored black by particles of soot, was precipitated in the cooler and condenser. The amount of liquid which could be obtained during one firing was about 200 g., enough to afford sufficient material for chemical investigation.

The following table shows the results of the analyses:

| Ingredients in 1 liter of water. | Ordinary firing in wood furnace May 4. | Biscuit-firing in gas furnace May 10. | Biscuit-firing in gas furnace May 11. | Ordinary firing in gas furnace May 16. |
|----------------------------------|--|---------------------------------------|---------------------------------------|--|
| Hydrochloric acid..... | .039 g. | .174 g. | .133 g. | .114 g. |
| Sulphuric acid | .153 " | .318 " | .408 " | .384 " |
| Phosphoric acid | .073 " | | | |
| Ferric oxide and alumina.. | .008 " | .022 " | | .017 " |
| Calcium oxide..... | .011 " | .062 " | | .039 " |
| Magnesium oxide..... | .008 " | .020 " | | .018 " |
| Potassium protoxide..... | .038 " | .096 " | | .037 " |
| Sodium protoxide..... | | | | .106 " |
| Ammonium chloride..... | | .128 " | | .047 " |

After the soot had been removed by filtering, the liquids appeared colorless and odorless with a decidedly acid reaction, the escaping non-condensable gases were odorless when wood was used in the firing, but when gas was used, there was an odor at times of sulphurous acid and at times of hydrogen sulphide, according as the flame in the furnace was oxidizing or reducing.

From this it will be seen that the precipitated liquids contain a number of substances which can even in a very dilute condition, produce a powerful chemical action upon the clay, since they penetrate into its pores by the aid of the water. These substances either cannot be volatilized alone, in which case it is to be supposed that they get into the furnace gas by dissociation, or they have a much higher evaporating point so that they are concentrated and have, for that reason, a more powerful action, and since evaporation takes place on the surface especially, their action is greatest on the surface. Aside from the substances which, it is supposed, made their way into the furnace gas by dissociation, the substances whose action we are to consider especially are alkaline sulphates, free sulphuric acid, free hydrochloric acid, and ammonium chloride. The first three must at all events increase the saltiness of the paste, either by remaining in it, or by combining the bases in it, alkalis, lime, magnesia, ferric oxide and alumina, and bringing them to the surface as saline incrustations, which can later be more or less decomposed again in a red heat and may disfigure the surface by incrustations or by a thin glaze.

The alkaline sulphates, which must be considered as acid salts when free acid is present, are known to be very powerful solvents for compounds of alumina and ferric oxide, and can even decompose a large number of their compounds insoluble in hot concentrated sulphuric acid; consequently these alkaline sulphates will also cause thorough decomposition in places where they can be deposited.

The ammonium chloride, which does not become volatile again under a temperature of 400 deg. C., has a similar decomposing action upon the silicates of the clay and may cause the formation of volatile chlorides of the calcium, magnesium, and iron, which, partially decomposed again when united with water, can be deposited in other places.

The presence of lime and magnesia, of alumina and ferric oxide, and also of hydrochloric acid, is perhaps due wholly or in part to the presence at the same time of ammonium chloride in minimum quantities in the products of combustion. At any rate, there

are many phenomena of colorations and discolorations which can easily be explained when it is shown that the above named substances are present in the furnace gas in sufficient quantity to be condensed.

The Process of Drying in the Open Air and in Enclosed Rooms Considered from a Theoretical Standpoint.

How to secure arrangements for drying which will make it possible to carry on the work of the brickyard in winter without interruption or at least with only moderate expense is a problem which has called forth communications and discussions from various sources. It cannot be said, however, that any solution of the problem has been reached which is at all satisfactory.

Some drying-houses are constructed in such a way as to utilize not only the heat radiating from the kilns standing within them, but also that escaping from the interior of the kilns after a firing. Others are provided with special heating appliances operated according to different systems. In some cases very ingenious contrivances for drying are in use, based on the principle of making the drying a continuous process, which shall keep pace with the molding upon the machine and the firing, a principle which has been successfully carried out in the firing process since the introduction of continuous kilns.

There are two scientific principles which have generally been disregarded in the construction of the drying plants in use at the present time: First, whether the drying is accomplished in the open air or in heated rooms, a very considerable amount of heat is consumed and becomes imperceptible to the senses during the process, as will be shown later by theoretical calculations: second, however great the amount of heat required theoretically, it is necessary to have great masses of air in motion to remove the vapors which are formed, especially if the drying must take place at a rather low temperature, and the nature of the material usually requires this.

In very many cases heating appliances have been erected at a great expense and have been found after all incapable of doing more than a part of the work expected of them. Even where the construction of the plant has permitted a forcing of the production of heat, the increased cost of the fuel has more than offset the advantage of continuing the work in cold weather.

It is probably only in those cases where the drying plants have been erected over kilns worked periodically. in which the

enormous amount of heat stored up in the walls and in the charge has been utilized, that it has proved feasible to dry enough raw wares by a part of this lost heat to maintain a regular operation of the works without apparent expense.

The attempt to solve the problem of winter operations on this basis has not yet met with success, and the drying which is claimed to be without expense is not so in reality. Such an operation cannot be carried on without expense any more than the working power can be supplied without cost, for it amounts simply to regaining in a somewhat crude manner and utilizing that which would otherwise be wasted in the free air. The amount of heat used, and in most cases injudiciously used, would not have to be produced at all if kilns were introduced which could be worked economically.

It is probably true that where special heating plants have been constructed for winter work, satisfactory results have been secured with artificial drying appliances only where the price of fuel is so low that a greater or less consumption of it makes no appreciable difference in the cost of production, or where other sources of heat are available which cannot be reckoned as lost heat.

Many who have introduced artificial driers have been astonished at the great consumption of heat, or in other words, at the unsatisfactory working of these driers and, supposing it to be due to the faulty construction of the apparatus, have tried to find something better, as the discussions on this subject in conventions have clearly shown. Yet a great consumption of heat is inevitable from the very nature of the case. The problem cannot therefore be solved for all cases or with any particular appliance, even with the most perfect one, but local conditions must in every case be taken into account in deciding whether artificial drying is advisable and profitable, or whether it is not better to utilize the heat of the sun in summer and artificial heat for the work in winter.

The laws of physics teach us that the transformation of a liquid into a gas or vapor requires a certain amount of heat imperceptible, however, to the thermometer, and to our senses, which is called the heat of vaporization or latent heat. For example, if water is heated in a vessel the temperature rises steadily to 100 degrees Centigrade, when the water boils—i. e., steam is given off in bubbles. The temperature of the water and of the evolved steam remains at 100 degrees Centigrade until the water is all vaporized. So the heat applied during this period is not able to raise the temperature of the water above 100 degrees, but is used up entirely in changing the condition of the substance and in replacing the

heat necessarily lost by radiation. The boiling ceases in fact as soon as the source of heat is removed.

The amount of heat required for this change of condition is definitely fixed and has been very exactly determined for the more important liquids by exceedingly delicate experiments. For water, the only liquid with which we are concerned in the study of the drying process, the amount of latent heat, plus that of the measurable free heat of the boiling water, equals 610 heat-units—that is, the same amount of heat which is necessary to heat 610 kg. of water from 0 deg. to 1 deg. C. is required to convert 1 kg. of water from 0 deg. into steam.

Transformation of water into steam takes place not only at the boiling point but at all lower temperatures, and even ice vaporizes; but at a temperature under 100 deg. vaporization takes place slowly from the surface of the liquid and is not accompanied by boiling and bubbling. This slow vaporization for which the presence of a medium is necessary to absorb and diffuse the vapors formed is called evaporation. Experiments made with the most accurate instruments have shown that the same laws prevail for the evaporation at lower temperatures as for vaporization in connection with the consumption of heat, and although the amounts of heat as determined by science for the formation of steam at different temperatures vary slightly, yet they may be regarded as equal for practical calculations. The number given above, 610, is therefore in general use for all temperatures, since this is the mean of several determinations.

Therefore, when water evaporates at 0 deg. it absorbs just as much heat as when it is vaporized at 100 deg.—i. e., 610 heat-units,—and without this absorption of heat evaporation is impossible.

This fixed relation between the quantity of water evaporated and the heat absorbed establishes a basis for a critical examination of the drying process; however, it is not the only factor to be taken into account here. As stated above, there is needed for evaporation a medium to carry off the vapors formed and to make possible the formation of new vapors. This medium is the air. The capacity of the air to absorb water vapor is limited and depends upon its temperature and pressure; yet it is found to vary primarily with the temperature, since the pressure as shown by the height of the barometer may be considered nearly constant.

When air can expand freely during the absorption of vapors, it is capable of absorbing at a given temperature so much vapor that its density, plus that of the absorbed vapors equals the pressure of the atmosphere as shown by the barometer.

The pressure of water vapors has been determined from 30 deg. C. upwards, and therefore the maximum amount of steam which the air can absorb at any particular barometric height and temperature can be calculated.

The accompanying table gives the figures of Prof. Magnus for the pressure of water vapor, expressed in millimeters, of a column of mercury at the temperatures with which we are concerned at present.

TENSION OF WATER VAPOR.
TABLE I.

| 0° C. | 4.525 Mm. | 11° C. | 9.751 Mm. | 22° C. | 19.675 Mm. |
|-------|-----------|--------|-----------|--------|------------|
| 1 " | 4.867 " | 12 " | 10.421 " | 23 " | 20.909 " |
| 2 " | 5.231 " | 13 " | 11.130 " | 24 " | 22.211 " |
| 3 " | 5.619 " | 14 " | 11.882 " | 25 " | 23.582 " |
| 4 " | 6.032 " | 15 " | 12.677 " | 30 " | 31.602 " |
| 5 " | 6.471 " | 16 " | 13.519 " | 40 " | 54.969 " |
| 6 " | 6.939 " | 17 " | 14.409 " | 50 " | 91.965 " |
| 7 " | 7.436 " | 18 " | 15.351 " | 60 " | 148.579 " |
| 8 " | 7.964 " | 19 " | 16.345 " | 70 " | 232.606 " |
| 9 " | 8.525 " | 20 " | 17.396 " | 80 " | 353.926 " |
| 10 " | 9.125 " | 21 " | 18.505 " | 100 " | 760.000 " |

At the mean pressure of the air—i. e., at a barometric height of 760 mm.—the amount of vapor which dry air can absorb at any given temperature is equal to the pressure of the vapor at this temperature (as given in the table above) divided by the pressure of the air. For example, at 10 deg. C. it equals $9.125 \div 760$ of its volume, or at 30 deg. $31.602 \div 760$ of its volume, and the composition of the moist air saturated with vapor is 9.125 parts vapor and $760 - 9.125 = 750.875$ parts of dry air at 10 deg., and 31.602 parts of vapor and 728.398 parts of dry air at 30 deg.

These illustrations will enable anyone to calculate without difficulty the capacity of the air to absorb vapor at any given temperature.

If one wishes to calculate from these statistics of volume the weights of water which one volumetric unit of air, e. g., one cubic meter, can absorb at a given temperature, the following formula may be used, the derivation of which I will not explain here, as it would lead to too many details.

$$G = 1,000,000 \frac{p}{(1+at)} \times \frac{p}{b}$$

In this formula

G = the weight of the maximum amount of vapor contained in one cubic meter expressed in grams.

S = specific gravity of the vapor o deg. C., and 760 mm. barometric height (computed at 0.000806 for water),

t = the temperature of the air,

a = the coefficient of linear expansion of elastic fluids = 0.003665,

p = tension of the vapor at the temperature (see table).

b = barometric height.

Therefore the amount of water which air at a temperature of 10 deg. C., and a barometric height of 760 mm. can absorb is

$$\frac{1,000,000 \times 0.000806}{(1 + 0.003665 \times 10)} \times \frac{9.125}{760} = 9.3 \text{ gr.}; \text{ at a temperature of 30 deg. C. and barometric height 760 mm.}$$

$$\frac{1,000,000 \times 0.000806}{1 + 0.003665 \times 30} \times \frac{31.602}{760} = 30.2 \text{ g.}$$

For practical purposes the barometric height may be regarded as constant at 760 mm. and the maximum amount of water which can be contained in one cubic meter of air can be calculated for the different temperatures by means of the formula given above, as follows:

| Tempera- ture. | Weight of Water in Grams in one Cu. Meter of Air. | Tempera- ture. | Weight of Water in Grams in one Cu. Mtr. of Air. |
|-------------------|---|-------------------|--|
| 0°C. | 5.4 grams. | 40°C. | 50.9 grams. |
| 5° " | 7.3 " | 50 " | 82.3 " |
| 1.0 " | 9.2 " | 60 " | 129.1 " |
| 15 " | 12.8 " | 70 " | 195.3 " |
| 20 " | 17.3 " | 80 " | 290.2 " |
| 25 " | 22.5 " | 100 " | 589.5 " |
| 30 " | 30.2 " | | |

If the amount of water to be vaporized and the temperature of the air charged with vapor are known, it is easy to calculate by means of this table the amount of air which must be carried off by some ventilating apparatus, whether this be a chimney or ventilator, or whether the movement of the air be brought about by leakages or by transmission through porous walls, and the intermediate values could be computed by means of the formula given above, if the air which is available for drying were absolutely free from vapors. In reality, however, this is not the case. Even if the atmospheric air seems for the most part quite clear and transparent, yet it always contains a considerable quantity of vapor, since it is always in contact with bodies of water and with the moist earth.

Cloudiness is not noticeable in the air until the latter has absorbed its maximum amount of moisture, and can no longer be dried. Consequently when its capacity for drying is to be considered, the amount of vapor contained in it must be taken into account.

When air containing vapor, but not completely saturated with it, is cooled, it reaches a certain point at which it contains the maximum amount of vapor possible, since its capacity to absorb vapor diminishes as the temperature is lowered, as the table given above shows.

If the cooling is accomplished below this point, a part of the vapor must be precipitated in liquid form, and this takes the form of rain, snow, mist, dew or frost, according to the quantity of the precipitation and the temperature.

The temperature at which air reaches its point of saturation for vapor is called its dew-point.

Air which has reached the point of saturation is incapable of absorbing more vapor unless it is rendered capable of it again by being warmed. Therefore misty air, which is saturated under all circumstances cannot be utilized as a drying agent, even when it is put into vigorous motion.

The amount of vapor present in the atmospheric air and influencing to a greater or less extent its capacity to serve as a drying agent, depends upon climatic conditions, upon the proximity of large bodies of water, upon the direction of the wind, the temperature of the air and earth, the season, etc. The amount of vapor—that is, its degree of moisture is measured by the hygrometer, or for practical purposes by the psychrometer.

This simple instrument consists of two ordinary mercury thermometers which are in agreement, fastened side by side upon a little board. The bulb of one of them is closely wound with muslin cloth, which is tied above and below the bulb and dipped into a small dish of water, by which means the bulb is kept moist. While the other thermometer shows the temperature of the air, this one, since its bulb is kept moist and is in an atmosphere saturated with vapor, for vaporization is in constant progress, indicates approximately the temperature at which the air is saturated with vapor,—i. e., the dew-point of the air.

If, for example, the dry thermometer shows the temperature of the air to be 15 deg. C., and the moist one shows the dew-point to be 10 deg. C., the amount of moisture in the air may be computed as follows:

According to Table I, the maximum amount of vapor possible at 15 deg. C. (and 760 mm. barometric height) is $\frac{12.677}{760}$ of the volume of the air. However, the real amount of vapor present is only that which corresponds to the saturation at 10 deg., i. e. $\frac{9.152}{760}$. The ratio of the two is therefore 12.677 : 9.125, or 100 : 72. We say that the air contains 72 per cent of moisture, i. e., 72 per cent of the maximum amount of water which it can absorb at the temperature noted. The actual amount of water which this air can still absorb can be computed by the formula given above or by Table II, which was derived from it.

One cubic meter of air can absorb at 15 deg. C. a maximum of 12.7 grams of vapor; the dew-point is 10 deg. C. It contains 9.2 grains of vapor. It can, therefore, still absorb 3.5 grams of vapor.

The amount of water contained in the atmosphere which determines its capacity for absorbing still more vapor varies according to local conditions and the season. At Halle, for example, systematic observations extending over long periods show the following mean:

The relative amount of moisture is: In January, 85.8 per cent; February, 81.0; March, 77.3; April, 71.3; May, 69.2; June 71.0; July 68.5; August, 66.1; September, 78.8; October, 78.9; November, 85.9; December, 86.8.

From this it can be seen that the atmospheric air can absorb in the summer months not more than one-third and in the winter months about one-eighth as much water as it can at the mean temperature of the single months, since over two-thirds or seven-eighths, respectively, of the amount of water are already present in it.

We are now in a position to study the process itself in the light of definite theories whose value can be determined.

DRYING IN THE OPEN AIR.

It has been demonstrated from experiments made by members of this association upon bricks which had been molded in machines operated on the systems most extensively used in Germany, namely, those of Schlickeysen, Sachsenberg and Hertel, that the average amount of moisture in freshly molded bricks taken from 25 machines is 24.9 per cent of the weight of the clay when dry.

A part of this water, 3.4 per cent, on an average, remains in the clay as hygroscopic water. It does not vaporize at ordinary temperatures and can be expelled only by the firing in the kiln at a

somewhat increased temperature. Consequently the water which is to be vaporized in the drying process amounts to 22.5 per cent of the weight of the clay when perfectly dry. For example, if the dry weight of 1,000 unburned bricks of full weight is 3,500 kg., 788 kg. of water must be evaporated, on an average, from every 1,000 bricks in order to obtain bone-dry bricks.

It is clear then from the demonstrations already given that the amount of heat absolutely necessary for evaporation, without which, indeed, no evaporation at all could take place, is 788×610 heat units = 480,680 heat units.

If this heat is to be secured by means of some kind of fuel, coal for example, which evolves in burning 7,500 heat units, on an average, the amount of coal required theoretically will be $480,680 \div 7,500 = 64$ kg., and in actual practice a much greater amount will be needed.

The question now arises: Where does the requisite heat come from when the evaporation takes place in the open air?

Every brickmaker has probably noticed the delightfully cool atmosphere which surrounds him when he walks between the stacks in a drying shed on a very hot day, or when he steps into a store-room in which bricks not entirely dry have been packed away, and he has doubtless observed also that a similar cool atmosphere is not perceptible between the stacks when the bricks have been thoroughly air-dried. He must have noticed, moreover, that there is no perceptible change of temperature in rainy weather, when the drying process is entirely stopped.

In fact, the rapid cooling of a moist body is always an indication that evaporation is in active progress and it is a well-known fact that the temperature may be appreciably lowered in summer by accelerating evaporation. This can be accomplished, however, only up to a certain point, which is fixed by the dew-point of the air by which the vapors formed are to be carried off. When this point has been reached the air cannot absorb any more vapor unless it is heated and thereby rendered capable of absorbing more vapor.

The rapidity of evaporation, that is, the amount of vapor absorbed by the air bears a fixed unvarying ratio to the lowering of the temperature which accompanies this process, so that a statement can be made of the equivalence between the loss of heat in the air and the amount of water absorbed in place of it.

Since there is a constant interchange of air between the interior of the drying sheds and the atmosphere without, it is evident that the heat lost by the air in the drying sheds must be regarded as the source of the heat consumed as latent heat in vaporization.

The air is therefore directly, and the heat of the sun indirectly, the source of the heat consumed as latent heat in the drying process.

In Berlin the mean temperature in summer is 17°C . The amount of heat contained in 1 cbm. of atmospheric air at 17°C . is equivalent to 5.542 heat units* or for each degree that the air is reduced in temperature it loses $5.54 \div 17 = .326$ heat units.

However, with an amount of heat equal to .326 heat units .534 gram of water can be vaporized ($1,000 \times .326 \div 610 = .534$).

Therefore, for every degree Centigrade lost by one cubic meter of air in passing through the drying plant there is an equivalent of .534 g. in the weight of water, i. e., whenever .534 g. of water are converted into vapor the cubic meter of air by which this vapor is absorbed and carried off loses 1°C .

The amount of heat absorbed by the bricks when there is a free circulation of air in the drying sheds depends not only upon the temperature of the air and the relative amount of water in it, but also upon the rapidity of its motion: upon the temperature, since the readiness with which the air gives up its heat in exchange for vapor increases with its removal from the point of saturation with vapor, i. e., with the removal of its temperature from the dew point; upon the rapidity of motion, since the air, which is the source of heat, furnishes the necessary amount of heat more quickly, the more rapidly it changes its place.

In order to gain some idea of the quantity of air necessary for drying in the open air under different conditions of moisture, we will assume that the temperature of the air is 17°C ., the dew-point 10° , and the velocity of the air such that it cannot be reduced 7° , but can lose only 3° in temperature in passing through the drying sheds, then every cubic meter will carry off, in compensation for the 3°C ., which are lost, an amount of water equal to $3 \times .534 = 1.602$ g. Since the amount of water to be vaporized is, according to the assumption made above, 788 kg. = 788,000 g. per 1000 bricks, the amount of air to be furnished by the wind for every thousand bricks in the drying sheds would be $788,000 \div 1.602 = 491,885$ cubic meters.

If, however, the air were, at this same temperature, 17° , near its saturation point for moisture, if, for instance, this point were at

*Let G equal the weight of one cubic meter of air at 0°C and 760 mm. pressure = 1.299 kg.

w = specific heat of the air = .2669;

t = temperature of the air;

a = coefficient of expansion of the air = .003665.

The amount of heat, W, can be obtained as follows:

$$W = \frac{G \cdot W \cdot t}{(1 + a \cdot t)} = \frac{1.299 \times .2669 \times 17}{(1 + .003665 \times 17)} = 5.542 \text{ heat units.}$$

16°C. and if the air could therefore cool off only .5° without reaching this point, then six times as much air would be needed to give off the heat and absorb the moisture.

It may be said that although heat is very desirable in drying bricks, yet the drying does progress rapidly even at a lower temperature, if the wind is blowing. This is true, but only when the air is not already completely saturated with water, for when saturated it is quite incapable of absorbing more vapors, even if it is considerably heated.

The theory has been advanced repeatedly in meetings of this association, that the particles of water which have not been transformed into vapor are carried off mechanically by the moving air, but this has not been demonstrated either scientifically or in practice.

It is immaterial in the drying process whether the air has originally a temperature of 17° or 10°C., if only the dewpoint is so far removed that the air can in either case give off the same amount of heat without reaching the saturation point as a result of this cooling.

Since there is never more than a slight amount of heat received by the air from the sun, the inexhaustible source of heat, and lost in vaporization, the amount lost varying according to the amount of moisture possible at a given temperature and that actually present, and since, under the most favorable circumstances, the quantity of heat given off never amounts to more than a few degrees, being often scarcely perceptible to the senses, a large quantity of air is always essential when bricks are to be dried in the open air and consequently the primary agent in open air drying is to be looked for in a free circulation of air.

DRYING IN INCLOSED ROOMS

presents different problems. Here the air introduced is not the only source for the heat lost in vaporization. Heat is supplied also by artificial means. Besides the disappearance of heat in becoming latent, an additional consumption of heat is made necessary by the circumstance that the moisture-laden air and the dried bricks have a higher temperature than the air and the bricks had when introduced into the drying room.

Let us suppose, for example, that the air laden with vapors is removed from the drying shed by means of some apparatus for ventilation at a temperature of 20°C., while it enters at a temperature of 4.5°C. (the mean temperature for the six winter and spring months in Berlin). The amount of heat carried off by the air in

this case, without having been used for drying, is found by calculation to be 4.89 heat units for each cubic meter* and the amount of heat required to heat the bricks also from 4.5° to 20° is 10,850 heat units per 1000 bricks.†

The air actually contains considerably less moisture in the winter, when only artificial drying apparatus can be used, than in summer, and it can therefore, when heated, absorb vapors more readily than at the same temperature in summer. Nevertheless the amount of heat required even in winter is very great, though by no means so great as that required for drying in the open air.

Suppose that during the winter and spring, the seasons when artificial drying apparatus is in use, the air is conducted into the drier at a mean temperature of 4.5°C., and that the amount of moisture in it is 80 per cent., on an average, in accordance with observations which have been taken. The water already contained in 1 cbm. is $6.25 \times .8 = 5$ gr.

*One cubic meter of air at 20° C., when saturated with vapor at a barometric height of 760 mm, contains in accordance with Table I.:

$$\frac{17.396}{760} \text{ vapor and } \frac{760 - 17.396}{760} = \frac{742.604}{760} = .974 \text{ cbm. dry air.}$$

The amount of heat can also be computed by the formula:

$$w = \frac{G \cdot w \cdot t}{1 + a} \text{ for 1 cbm. of dry air at 20° C.}$$

or

$$w = \frac{G \cdot w \cdot t}{(1 + a)} \times .974 \text{ for 1 cbm. of moist air at 20° C.}$$

that is

$$\frac{1.299 \times .2669 \times 20}{(1 + .003665 \times 20)} \times .974 = 6.31 \text{ heat units.}$$

The above mentioned .974 cubic meters of air at 20° when entering the drying house at 4.5°, a temperature lower by 15.5°, occupied .914 cbm. of space

$$\left(\frac{.974}{1 + .003665 \times 15.5} = .914 \right) \text{ or, when saturated with vapor at 4.5°, .922 cbm}$$

$$\left(914 \times \frac{760}{760 - 6.25} = .922 \right)$$

The heat capacity of this amount of air at 4.5° is $\frac{1.299 \times .2669 \times 4.5}{1 + .003665 \times 4.5} \times .922 = 1.42$ heat units.

The difference between 6.31 and 1.42 gives the amount of heat carried off from the drying house at 20°; that is, 4.89 heat units.

†Let 3500 kg. represent the weight of 1,000 bricks:

0.2 the specific heat of the clay:

15.5° the difference in temperature.

The amount of heat will then be $3,500 \times .2 \times 15.5 = 10,850$ heat units.

‡The volume of the air when heated can be computed by the formula:

$$v_1 = v \times (1 + a[t - t_1]) \text{ in which}$$

v = the original volume.

v_1 = the volume after expansion.

a = the coefficient of expansion for the air = .003665.

$t - t_1$ = the difference in temperature.

Since the amount of moisture remains invariable it decreases in each cubic meter in proportion as the volume increases by expansion; we obtain therefore:

$$G_1 = \frac{G}{1 + a(t - t_1)} \text{ in which}$$

G represents the original weight of the water.

G_1 the weight of the water after expansion.

The same air when heated to 10° , and thereby expanded, would contain in each cubic meter 4.9 g. of moisture; at 20° C., 4.7 g.; at 30° C., 4.5 g.; at 40° C., 4.4 g.

If these expressions for the amount of moisture are subtracted from those which 1 cbm. of air can contain as a maximum, at the temperatures in question (see Table I.) the quantity of moisture will be obtained which the air has absorbed from the bricks to be dried, supposing that this same air has been conducted out of the drier, completely saturated with moisture.

The amount of moisture is as follows:

TABLE III.

For each cubic meter of moist air

| | | |
|--------------------|--------------|-------------------|
| At 10° C. | $9.2-4.9=$ | 4.3 grams water |
| At 20° C. | $17.3-4.7=$ | 12.6 grams water |
| At 30° C. | $30.2-4.5=$ | 25.7 grams water |
| At 40° C. | $50.9-4.4=$ | 46.5 grams water |
| At 50° C. | $82.3-4.2=$ | 78.1 grams water |
| At 60° C. | $129.1-4.1=$ | 125.0 grams water |
| At 70° C. | $195.3-3.9=$ | 191.4 grams water |
| At 80° C. | $290.2-3.8=$ | 286.4 grams water |

The amount of air required to carry off in the form of vapor the water contained in 1000 bricks, that is, 788 kg=788,000 'g., is as follows:

| | | |
|--------------------|-----------------------|--------------|
| At 10° C. | $788,000 \div 4.3=$ | 183,256 cbm. |
| At 20° C. | $788,000 \div 12.6=$ | 60,952 cbm. |
| At 30° C. | $788,000 \div 25.7=$ | 30,661 cbm. |
| At 40° C. | $788,000 \div 46.5=$ | 16,946 cbm. |
| At 50° C. | $788,000 \div 78.1=$ | 10,090 cbm. |
| At 60° C. | $788,000 \div 125.0=$ | 6,304 cbm. |
| At 70° C. | $788,000 \div 191.4=$ | 4,117 cbm. |
| At 80° C. | $788,000 \div 286.4=$ | 2,751 cbm. |

It is evident that while the amount of air required for carrying off the vapors in a drier decreases rapidly as the temperature rises, it is nevertheless very considerable even at a moderately high temperature.

Attention has already been called to the fact that the consumption of heat in artificial driers is not limited to the amount of heat

which becomes latent when the state is changed, i. e., that which is required merely for the vaporization of the water, but a consumption of heat is also involved in the fact that the air laden with moisture has a higher temperature when it escapes than it had before and the dried bricks have this higher temperature likewise. If these factors are taken into consideration, the total consumption of heat can be computed as follows: We will assume that the moist air is conducted away at 20° C. We have seen that 1 cbm. of air has to absorb 4.89 heat units in order to be changed from 4.5° to 20° C. We have also found that at this temperature 60,952 cbm. of air are required to vaporize and carry off the water from one thousand bricks = 788 kg. The heat carried off by this air is therefore $60,952 \times 4.80 = 298,055$ heat units.

The latent heat of 788 kg. of vapor equals $788 \times 610 = 480,680$ heat units. The $11,850 \div 790,585$ heat units required to heat the clay represent in all a consumption of coal equal to $790,585 \div 7,500$, which equals in round numbers 105 kg. of coal per 1,000 bricks.

Since some heat is inevitably wasted this theoretical consumption of coal will always be considerably greater in practical operations.

Clearly the consumption of coal is not so great in itself as to make the erection of drying plants for this reason alone impracticable, provided sufficient care is taken in the construction of the drying apparatus to avoid as far as is possible the wasting of heat. This is very difficult, to be sure, but it is much more difficult, as can be seen from the computation of the amount of air needed, to bring about the circulation of air which is needed to carry off the vapors formed at a comparatively low temperature. When the drying takes place in the open air this task is performed satisfactorily by the wind; in inclosed rooms this is of course impossible and some sort of drying apparatus must be used, perhaps a flue or a bellows. This seems to be the weak point in the winter driers which have been constructed up to the present time.

It may be thought that ventilation can be secured simply by openings in the roof of the drying room and it is true large quantities of air can escape in this way but there is danger that much air will be removed before it is completely saturated with vapor, since such an arrangement for ventilation would be disturbed to a great extent by the circulation of the air outside.

It is possible to dry large quantities of wares in inclosed rooms only when a large amount of heat which would otherwise be wasted can be utilized, as is the case for instance in the driers erected over periodic kilns or over the Mendheim gas furnaces. But if special heating plants must be set up to supply heat for the driers, there

must be also some ventilating apparatus which can be controlled, in order to avoid the excessive consumption of coal in the heating apparatus with only moderate results in the way of drying.

In order to get an idea of what may be expected when ventilation is accomplished by means of a flue, let us compare the volumes of air as already determined with those which would be required in burning an equal number of bricks in an annular kiln. In the latter case there are required only about 3,100 cbm. of air at 40° C., assuming that 200 kg. of coal are used in the burning (Cf. Notizblatt, 1875, page 180), that twice as much air is supplied to the fire as is necessary for burning, and that the wares are put into the flue at a temperature of 40° C.

It is clear that the amount of air needed for drying is much greater than that needed for burning the same number of bricks. At a drying temperature of 40° C. five times as much air must pass through the flue as would be necessary in burning; at 30°, ten times as much; at 20°, twenty times as much; not until the temperature is raised to 70 or 80° C. is the amount small enough to correspond to the capacity of a flue of moderate dimensions.

In order to understand better the significance of the table giving the amounts of air theoretically needed for drying, let us imagine a plant in which 5,000 bricks are burned daily in an annular kiln. Experience has shown that the stack needed to produce the required draft in such a plant would have to be 25 m. high with a clear opening of 8 m. at the top. Suppose a like stack is built in the drying plant which supplies the annular kiln with 5,000 bricks daily for the purpose of ventilating the drying room. The drying plant is, we will assume, the most perfect one imaginable, and the amount of coal and air used corresponds exactly to the theoretical consumption. If we then calculate the efficiency of such a stack* we find that the quantities of air it carries off are as follows:

*Let $t-t_1$ represent the difference in temperature between the inside of the stack and the air outside;
stack d_1 the diameter at the mouth;
 h , the height.

The products of combustion will come from the stack with the following velocity:

$$v = 628 \sqrt{\frac{(t-t_1) \times d \times h}{4.08 + .016h}} \text{ meters per minute.}$$

The quantity of air per minute is as follows:

$$V = \frac{\pi \cdot d^2}{4} \times v = \frac{\pi \cdot d^2 \cdot 628}{4} \times \sqrt{\frac{(t-t_1) d h}{4.08 d + .016 h}}$$

or in 24 hours.

$$\frac{\pi \cdot d^2 \times 6.28 \times 24 \times 60}{4} \times \sqrt{\frac{(t-t_1) d h}{4.08 d + .016 h}}$$

These are the formulae by which the table is obtained (Cf. Ing.-Taschenbuch 1870, p. 445.)

With an outer temperature of 4.5° C. and an

| | Per Min. | In 24 hrs. |
|---------------------------------|------------|--------------|
| Inner temperature of 20° C..... | 30.5 cbm. | 43,920 cbm. |
| Inner temperature of 30° C..... | 38.4 cbm. | 55,440 cbm. |
| Inner temperature of 40° C..... | 45.9 cbm. | 66,096 cbm. |
| Inner temperature of 50° C..... | 52.3 cbm. | 75,212 cbm. |
| Inner temperature of 60° C..... | 59.6 cbm. | 85,824 cbm. |
| Inner temperature of 70° C..... | 64.8 cbm. | 93,312 cbm. |
| Inner temperature of 80° C..... | 69.55 cbm. | 100,080 cbm. |

The two tables showing the quantities of air required to absorb and carry off the vapors formed at different temperatures, and also the one showing the capacity of a stack, are of great value in our discussion, since they demonstrate the fact that when a stack is used the masses of air which are to be set in motion cannot be controlled unless the drying takes place at a moderately high temperature, say at a minimum of 40° C.; at a lower temperature a stack of enormous dimensions would be required, or else an exhaustor would have to be used and this would necessitate again such a great consumption of force and heat as to counteract the advantages of operating a drying plant in winter.

This much at least has been made clear by the tables, that these driers can be easily managed and made to correspond in efficiency with the other processes of the industry only when the higher temperatures are secured in the driers themselves and in the vapor-laden air which passes out from them, for the difficulties in securing thorough ventilation diminish as the temperature is increased. And not only the amount of air to be set in motion, but also the amount of heat consumed is less in proportion as the temperature of the moist air which passes off is increased. This sounds paradoxical, but the fact is fully established. The relative amount of heat taken off by the air is, to be sure, greater at a higher temperature, since it increases as the temperature rises, yet the absolute amount of heat in the air is much greater at a lower temperature, because the volume of air required increases rapidly as the temperature decreases.

It is true that the unintentional waste of heat, which we have left out of the account in our discussion, increases also as the temperature in the drier rises, yet it seems easier in practice to make amends for lost heat than to overcome the disadvantages of faulty ventilation.

When the drying takes place at a low temperature, below 30°, a larger drying room is required, and is usually utilized for other

processes also, in which curiously enough, no attention is paid to ventilation, although theoretically very thorough ventilation is demanded. It is only by means of porous walls and necessary openings that even a small fraction of the necessary change of air is secured; an effort is even made to keep every breath of cold air from penetrating into the room, for fear that the little bit of heat which has been secured will be lost, although scarcely enough has been secured to make the temperature endurable and by no means enough to vaporize any great amount of water.

It must be borne in mind, that the theoretical consumption of heat, which we may look upon as representing the minimum consumption of coal under ordinary circumstances, amounts to two-thirds of that used in a well-built annular kiln for the final burning of the bricks and the actual consumption in most cases probably equals or exceeds it.

Therefore any winter drying plant which is expected to dry a large number of bricks must have the drying rooms heated enough to warm the air perceptibly even with good ventilation, and if the necessary heat and ventilation are not present, the efficiency of the plant will be very slight. Indeed it can be seen in the majority of the brickyards arranged for winter work that the material secured from driers heated by artificial means furnishes only a small proportion of the dried products which a continuous kiln in regular operation can produce.

Although there is ample justification in theory for the construction of driers which can be operated at a high temperature, not exceeding 100° however, very few have as yet been built, and it is only in the last few years that an impetus has been given to experiments in this direction. Little or nothing is known as yet of the results obtained where the driers of Weigelin, Ruhne and Bock are employed.

In drying at a high temperature the aim will be, naturally, to secure compact apparatus and a short period of drying, that is, more rapid drying, but at the same time it will always be a practical question of great importance, whether the raw material is of a nature to permit rapid drying. Nevertheless the difficulties in this respect are perhaps greater than is commonly supposed.

Many of our brick experts are engaged at the present time in constructing drying apparatus, but it must be said that the builders of most of the plants constructed heretofore have in their ignorance of the natural laws concerned disregarded them to a great extent.

In presenting the considerations of this present article my purpose has been not to find fault with the different systems now in

use, but merely to examine into the merit of the driers which have been constructed and to furnish statistics which may serve as a basis in calculating the dimensions of apparatus for heating and ventilating.

The Theory of "Watersmoking" in the Annular Kiln.

At the last general meeting of the "German Association of Manufacturers of Tiles, Pottery, Lime and Cement" (Deutscher Verein für Fabrication von Ziegeln, Thonwaaren, Kalk und Cement), the subject of watersmoking in the annular kiln was discussed at great length.

Reports were presented giving the results of experience with smoke-flues, by means of which the warm air required for watersmoking is conducted from the cooling chambers of the kiln to those in which green wares have been set, and also with various kinds of small portable furnaces which have been used successfully, it was claimed, in watersmoking in the annular kiln.

Mysterious allusions were made also to new apparatus and new methods which were said to insure the highest possible degree of safety and economy in the watersmoking process in continuous kilns.

One feature of the new method was said to be the separation of the watersmoking from the actual advance warming and firing processes. This method of procedure has, by the way, been repeatedly urged upon manufacturers using annular kilns during past years, but it is practiced unfortunately in only a few cases. But the chief merit of this improved process consists, it was claimed, in the removal of the vapors formed in watersmoking in the most "natural" way; that is, through the openings in the arched roof of the furnace, the "natural tendency" of vapors to rise being thus turned to account in their removal.

It is true of course that the specific gravity of aqueous vapors is less than that of the air, under the same pressure and at the same temperature, and vapors formed under atmospheric pressure, i. e., 100° C., do therefore rise in the air, but notwithstanding this, it is nonsense to talk of the "natural tendency of the vapors to rise" in connection with the watersmoking process. Vapors are formed only when heat becomes latent at the same time, and to vaporize a fixed amount of water there is required a fixed amount of heat which can be expressed in figures. These two factors, the vapor formed and the heat consumed, stand in a fixed relation to each other.

Since the air, in whatever way it is warmed, is always to be considered the carrier of the heat in the watersmoking process, it contains in its unit of volume at any easily determined temperature a certain amount of heat, which can be used for forming vapors from liquid water. Now it can very easily be determined how much vapor can be formed with this heat and how much the air is cooled by the loss of this same heat. We find that the contraction of the air on account of this loss of heat is considerably greater than the increase in volume which it gains by mingling with an amount of vapor equivalent to the lost heat, therefore the air already used for watersmoking and cooled by this process has gained a greater specific gravity than the dry but warmer air which enters the kiln at the beginning of the process.

If now the air does, as a matter of fact, rise, it is not due to any mysterious innate tendency, but to the fact that the heat carried by the air is not entirely exhausted and the air contained in the furnace is therefore warmer and lighter than the free atmosphere. If this air in the furnace with its lesser specific gravity is mingled directly with the outer air it does rise in the furnace, but if it mingles with the still warmer air in the chimney of the annular kiln, its natural course is downwards.

In the former case a certain amount of heat must be left in the air, in the latter case, the rapidity of the motion of the air will increase as its heat is taken from it, i. e., as the difference of temperature between the air at the bottom of the furnace and that in the chimney is increased, the air in the chimney having its draft supplied from a different source of heat.

Just as the air inside of a vertical tube moves upward when it is heated more than the outside air, and downward when it is cooled, so here the action of the furnace chimney is reinforced by an inverted chimney, as it were, of the height of the furnace chambers, when a current of warm air is introduced beneath the arched roof for watersmoking and is robbed of its free heat during the watersmoking process.

As long as the temperature of the water evaporating in the smoking chamber remains below 100° C. there is no separation of the vapors from the air in which the vapors have been formed; therefore the vapors have no occasion to escape from openings in the top of the kiln alone and in no case to any greater extent than, would correspond to the amount of air needed to keep the vapors in solution and to the temperature which determines the capacity of this air to absorb vapors.

Experiments have shown that gases formed in a space already filled with another gas are diffused in it according to the same laws as in a vacuum, that is, they are distributed evenly within this space, but the diffusion is slower than in a vacuum owing to the resistance offered by the gas already present. When such a mixture has once taken place (and in the watersmoking process it must take place as soon as the vapor is formed, since each molecule of air has to give up its heat to a molecule of water in order to make the formation of vapor possible) there is no separation again according to specific weights, but the gases always act toward each other like perfectly miscible fluids (as, for example, alcohol and water) and not like immiscible ones (as, for example, oil and water). Therefore the air in the upper part of the furnace can not contain more moisture than that in the lower part unless its temperature is higher and its capacity for absorbing vapor greater; but if the air below is warmer, then the moisture will be greater here.

Before passing to a detailed discussion of the phenomena which appear in connection with watersmoking, and to a presentation of statistics with regard to the various modifications of these phenomena which occur in actual experience, I wish to review once more the fundamental principles of watersmoking, because I believe that many erroneous views are held with regard to this process.

Anyone who has examined analyses of clay must have noticed that chemically combined water is always mentioned in them, the amount varying from 2 to 15 per cent in different kinds of raw material. This water cannot be removed by continued drying. It escapes only when the temperature is raised. A red heat is required to drive it off, and its expulsion is indicated in most cases by a change in the color of the clay.

The expulsion of this water is the chemical process which forms the real aim in the firing of the clay.

When clay is moistened with water and made plastic, it loses the greater part of this water again by vaporization. A part of the water, however, remains tenaciously in the pores of the clay and cannot be driven off by drying at ordinary temperatures, but only by heating to a point above the boiling point of water, to about 120° C.

On the other hand, clay dried at 120° C. and exposed to the air at ordinary temperatures, absorbs this amount of moisture from the atmosphere again. This water varying in amount from 1 to 8 per cent is called hygroscopic water and the object of the

so-called "watersmoking" is to drive off this water as well as any water which may be left in the clay as the result of imperfect drying. The process of watersmoking is ended therefore when all parts of the wares in the kiln have reached a temperature a little above 100° C.

In order to expel the hygroscopic water a definite amount of heat must be supplied, and this heat must be absorbed in order to convert the water into steam.

In actual practice this heat is always supplied by means of a current of heated air. A special fire may be used to produce this current, or the air may be heated by being passed over bricks already fired by means of a smoke flue and chimney, or the heated furnace gases escaping after the firing may be utilized.

From an economical standpoint it seems at first sight most practicable to utilize the source of heat last mentioned, but we shall see later that at the temperatures at which the hygroscopic water must be expelled the furnace gases are most unsuited to this purpose.

The amount of steam which atmospheric air can absorb is limited and is determined by its temperature. The higher the temperature of the air the more it can absorb, until the temperature reaches and exceeds 100° C., when the amount of vapor does not depend upon the amount of air, so that from this point on unlimited quantities of vapor can be absorbed.

Now since the smoking process, as was said above, is ended at 100° C., it is of especial importance to determine the capacity of the air to carry off vapors at the temperatures below 100° C.

Water evaporates at any temperature, at 0° C. as well as at the boiling point, but the pressure at which the vapors are formed varies greatly. The pressure of the different kinds of air is measured by the barometer. The pressure of the atmospheric air is expressed by the height of a column of mercury averaging 760 millimeters in length; the pressure of water vapors at different temperatures has been determined by experiments. At 100° C. it is equivalent to that of the air, or 760 mm.; at 50° C. it is 88.7 mm.; at 20° C. 17.3 mm.; at 0° C., 5.1 mm.

The maximum amount of vapor which the air can absorb at a given temperature corresponds to this pressure as follows:

At 0° C. the vapor contained in the air is 5.1-760 of its volume; at 20° C. it is 17.3-760, and at 50° C. 88.7-760, and the air can absorb vapor only in this proportion until this maximum is reached.

If then air containing less vapor than is required for saturation

at this point is cooled, it will reach a temperature eventually at which it is able to barely hold the vapors in solution. This point is called the dew-point of the air, because below it a part of the vapor is precipitated in liquid form as dew.

The determination of the dew-point is of especial importance in our discussion, because it indicates the temperature which the air must have if it is capable of being used at all in drying and watersmoking. It must never be cooled below this point during the watersmoking, because the coloring of the wares to be burned is endangered if they are covered with dew. This is of the greatest consequence if the gases which pass off from the fire are used for watersmoking, since these already contain a great quantity of vapor and other injurious substances which are derived from the clay while the latter is being fired.

In the manufacture of the most common brick wares the qualities most desired are form, firmness, and resistance to atmospheric influences, but if wares of better quality are to be produced, it is absolutely necessary that a uniform coloring be secured in addition to the above mentioned qualities. In the latter case therefore especial attention should be given to the watersmoking since the skill shown in the execution of this process is an important factor in securing a perfect firing.

It has been clearly shown on previous occasions that the conditions for securing a uniform surface coloring are much more unfavorable in all varieties of continuous kilns, of whatever construction and whether solid fuel or gas is used in them, than in periodic kilns. There are two reasons for this: first, in continuous kilns the air which has to carry off the vapors from the green bricks is limited in quantity by considerations as to advantageous firing and economy in the consumption of fuel, and second, the furnace-gases of continuous kilns contain more moisture, and are therefore less capable of absorbing vapors than the air supplied from without for watersmoking in the periodic kilns.

Surface colorations are correctly attributed in a great majority of cases to the fact that deposits from the furnace-gases are formed upon the cold surfaces of the bricks. In connection with the vapors there are deposited volatile alkali salts, acid vapors, and flue-dust, which leave behind on the surface, after the water has disappeared, a saline efflorescence or a deposit of ashes, or more correctly speaking, the chemical composition of the clay is altered to a greater or less depth from the surface and consequently its color is changed.

Phenomena which might be attributed to the action of the fur-

nace-gases upon the bricks at the moment when the heat is greatest do not occur except in rare cases and under special conditions. It has been claimed that changes in color are caused by the faster or slower cooling of the bricks, but there has never been any attempt to demonstrate this on scientific principles. The theory seems to have been invented for the sole purpose of illustrating the superior points of particular systems.

Abundant proof has been furnished in continuous systems, especially in the annular kiln, that if discolorations have not arisen during the drying process from saline efflorescence they do not occur during the burning process, since there is no opportunity here for the precipitation of water and in connection with it of the other injurious matters contained in the furnace-gases.

The danger that the brick wares will become softened, cracked or dissolved during the watersmoking increases in proportion as the air introduced for watersmoking becomes less able to absorb and carry off vapors rapidly, that is, in proportion to the amount of vapor it contains as it comes from the firing.

If we except the cases in which vapors are introduced, on account of faulty insulation, when moisture is present to begin with, as, for example, in a badly constructed kiln, we find that the amount of vapor in the air depends upon three things: upon the amount of water or hydrogen in the fuel employed; the amount of chemically combined water in the clay, which is expelled in the firing; and the amount of the so-called hygroscopic water remaining in perfectly air-dried clay.

If then it is desirable to reduce the amount of vapor in the furnace-gases, this can be regulated to a certain extent by the choice of fuel, since fuel which is perfectly dry or which has at the outset little water or hydrogen can be employed. But the moisture of the clay cannot be regulated, assuming of course, as a fundamental principle, that the material employed has in every case been perfectly air-dried.

The statistics which follow are intended to serve a two-fold purpose: first to give an idea of the effect which the composition of the clay and the quantity of the material to be burned have upon the composition of the furnace-gases, and consequently upon the watersmoking process; and, secondly, to show the amount of heat and air necessary to insure complete success in the watersmoking process in all cases.

I.—The Humidity of Furnace Gases.

The statistics presented here are based upon the analysis of three varieties of non-calcarous brick clay, which differ as much as possible from each other in the amount of chemically combined and hygroscopic water contained in them. The clays are as follows:

1. Brick-clay from Schwarzhütte, near Osterode am Harz.—Containing 2.5 per cent of chemically combined water, and 2.6 per cent of hygroscopic water (compared with burned clay as a standard).
2. Clay from the Siegersdorf Brick Works in Siegersdorf.—Containing 5 per cent of chemically combined water, and 4.8 per cent of hygroscopic water.
3. Clay from the Greppin Brick Works, near Bitterfeld.—Containing 10 per cent of chemically combined water and 6.4 per cent of hygroscopic water.

It must be understood in the first place that all these clays were air-dried when used and were burned in an annular kiln with the same amount of coal, that is, 200 kilograms of coal of medium composition per thousand bricks.* The composition of the coal is as follows:

| | |
|----------------|---------------|
| Carbon | 78.0 per cent |
| Hydrogen | 5.2 per cent |
| Oxygen | 11.8 per cent |
| Ashes | 5.0 per cent |

Suppose just enough air is supplied to the fire to convert the carbon into carbon-dioxide† and the hydrogen into vapor. The necessary amount of air can be computed as follows:

156 kilograms of carbon consume 416 kg. oxygen, and produce 572 kg. carbon dioxide;

7.4 kilograms of hydrogen consume 59.2 kg. oxygen, and produce 66.6 kg. vapor.

The remaining 3 kilograms of hydrogen unite with the 23.6 kg. oxygen contained in the coal and produce 26.6 kg. vapor.

*According to Prof. Blaschke, the mean average of the analyses of 67 varieties of coal, after the ashes have been deducted, is as follows:

| |
|------------------------|
| Carbon 82.1 per cent. |
| Hydrogen 5.5 per cent. |
| Oxygen 12.4 per cent. |

If we add 5 per cent ashes, we obtain the figures given above.

†Six parts by weight of carbon unite with 16 parts by weight of oxygen to form 22 parts by weight of carbon dioxide; 1 part by weight of hydrogen and 8 parts by weight of oxygen make 9 parts by weight of vapor.

The amount of atmospheric oxygen consumed is therefore 475.2 kg., or, since 1 cbm. oxygen weighs 1.4323 kg. at 0°C. and 760 mm. barometric pressure, 331.8 cbm. oxygen for 200 kg. coal.

But the air which enters the kiln contains nitrogen as well as oxygen, 79 parts of volume of nitrogen to 21 parts of volume of oxygen,

To correspond to the 331.8 cbm. of oxygen there must be present therefore 1248.2 cbm. of nitrogen, so that the entire volume of air which is just sufficient to burn 200 kg. of coal of the above composition amounts to $331.8 + 1248.2 = 1580$ cbm.

Let us see what results from the burning.

| | Cbm. |
|---|-----------|
| Nitrogen remaining unchanged..... | 1248.2 |
| The 572 kg. of carbon dioxide which are derived from the carbon, as explained above, occupy in space..... | 288.6 |
| The elements of the water in the coal furnish 26.3 kg. vapor, which equals.... | 33.2 cbm. |
| The burning of the excess of hydrogen gives 66.6 kg. vapor, which equals..... | 82.7 cbm. |
| | 115.9* |

Total of products of combustion.....1652.7 cbm.

To these products of combustion the vapor must be added which is formed in the red heat from the chemically combined water in the clay. Assuming the weight of the burned bricks to be 3 kg., the amount of vapor formed is as follows:

In the clay from Schwarzhütte (2½%)..... 75 kg.= 93.1 cbm.
 In the clay from Siegersdorf (5%).....150 kg.=186.2 cbm.
 In the clay from the Greppin Works (10%)....300 kg.=372.4 cbm.

An analysis of the furnace-gas formed during the combustion of 200 kg. coal results as follows:

CHEMICALLY COMBINED WATER.

| | 2½% | 5% | 10% |
|----------------------|-------------|-------------|-------------|
| Nitrogen | 1248.2 cbm. | 1248.2 cbm. | 1248.2 cbm. |
| Carbon dioxide | 288.6 cbm. | 288.6 cbm. | 288.6 cbm. |
| Vapor | 209.0 cbm. | 302.1 cbm. | 488.3 cbm. |
| | 1745.8 cbm | 1838.9 cbm. | 2025.1 cbm. |

or, expressed in percentages,

*The standard used for these volumes is the one usually used in measuring gases, the space occupied by a gas at a temperature of 0°C. and a barometric height of 760 mm.

CHEMICALLY COMBINED WATER.

| | 2½% | 5% | 10% |
|----------------------|-------------|-------------|-------------|
| Nitrogen | 72.5 | 67.9 | 63.6 |
| Carbon dioxide | 16.5 | 15.6 | 14.5 |
| Vapor | 12.0 | 16.5 | 21.9 |
| | <hr/> 100.0 | <hr/> 100.0 | <hr/> 100.0 |

Now the dew-point of the furnace-gas must be determined, that is, the point at which it is able to contain the water in the form of vapor and conduct it away. The pressure of the air which passes off may be assumed, with sufficient accuracy for our purpose,† as equivalent to the pressure of the atmosphere without, that is, a barometric height of 760 mm. The various constituents share in this pressure in proportion to their volumes. Therefore the pressure of the vapors in the furnace-gas is as follows:

In the clay containing 2½% water, $760 \times .12 = 91.2$ mm. bar. height.

In the clay containing 5% water, $760 \times .165 = 128.4$ mm. bar. height.

In the clay containing 10% water, $760 \times .219 = 166.4$ mm. bar. height.

The dew-point of the air coincides with the temperature at which water boils under a given pressure. We know from experiments made by Dulong that the boiling point for water is

100°C. when the steam pressure is 760 mm.

50°C. when the steam pressure is 91.2 mm.

57°C. when the steam pressure is 128.4 mm.

63°C. when the steam pressure is 166.4 mm.

This means, expressed in practical terms: As soon as the bricks in the watersmoking chambers have been heated by any means (under the conditions upon which our calculation is based) to a temperature of 50°C. (when 2½% of chemically combined water is present), 57°C. (5% chem. comb. water), or 66°C. (10% chem. comb. water), it is impossible for the vapors to be separated from the furnace-gas which is used for watersmoking; on the other hand, if the temperature of the bricks falls below the temperatures just given, water will always be precipitated. Take the clay from Greppin for example. Suppose the furnace-gas is cooled to 50°C. through contact with the cold bricks. Since in the amount of furnace-gas calculated for 1,000 bricks, 389.9 kg. of vapor can be held in solution at 66°C., but only 183 kg. at 50°, water must be pre-

†A number of tests made in the smoke-flue of the Kalk annular kiln of Herr Friedr. Hoffmann, Nordhafen, Berlin, showed that the maximum refraction of the air was 14.22 mm. hydrostatic pressure, which equals 1.05 mm. mercury under ordinary atmospheric pressure.

cipitated here in liquid form to the amount of 206.9 kg., or nearly 7 per cent of the weight of the burned bricks.

The precipitations of water must diminish more rapidly as the dew-point of the furnace-gases is lowered, because the capacity of the air to absorb vapors increases very rapidly as the temperature rises, as can be seen from a glance at the temperatures given above and the corresponding quantities of water held in solution.

It has been assumed in the above calculation that the amount of air used in firing was only just sufficient to convert the coal into carbon dioxide and water. In practical operations, however, this proportion cannot always be observed. Schinz states that this end cannot be attained in practice unless gas is used for fuel, in which case no obstacles prevent the rapid and thorough mixture of fuel and air, whereas if solid fuel is used, which presents less surface to the contact of the atmospheric air, it takes, on an average, twice the amount of air theoretically required to produce smokeless combustion.

Unfortunately we are not yet in the possession of analyses of furnace-gases in the annular kiln which might enlighten us on this point. It is expected that light will be thrown upon the subject by a series of experiments with the Orsat apparatus for the analysis of air, which were described by Herr Dr. Jul. Aron at the last general convention of the German Association of Manufacturers of Bricks, etc.

The statement of Schinz refers only to grate firing, but it is to be assumed that the consumption of air in the annular kiln will be somewhat between the two extremes already mentioned. Let us therefore examine as the second extreme the conditions which arise when the quantity of air drawn in by the chimney for the purpose of burning the coal is twice as great as is necessary. We will suppose then that 1,000 bricks are to be burned with 200 kg. of coal, and that 3160 cbm. of air are supplied for this purpose instead of 1582 cbm. In this case half of the air will serve merely to produce rarefaction and the analysis of the furnace-gas will result as follows:

CLAY CONTAINING WATER.

| | 2½ % | 5 % | 10 % |
|----------------------|-------------------|-------------------|-------------------|
| Nitrogen | 2496.8 cbm. | 2496.8 cbm. | 2496.8 cbm. |
| Carbon dioxide | 288.6 cbm. | 288.6 cbm. | 288.6 cbm. |
| Vapor | 209.0 cbm. | 302.1 cbm. | 488.3 cbm. |
| Oxygen | 331.8 cbm. | 331.8 cbm. | 331.8 cbm. |
| | <hr/> 3326.2 cbm. | <hr/> 3419.3 cbm. | <hr/> 3605.5 cbm. |

This expressed in percentages is:

| CLAY CONTAINING WATER. | | | |
|------------------------|-------|-------|-------|
| | 2½% | 5% | 10% |
| Nitrogen | 75 | 73 | 70.5 |
| Carbon dioxide | 8.7 | 8.5 | 8.0 |
| Vapor | 6.3 | 8.8 | 12.3 |
| Oxygen | 10.0 | 9.7 | 9.2 |
| | <hr/> | <hr/> | <hr/> |
| | 100 | 100 | 100 |

From this analysis we can compute in the case of each material the tension of the vapor and the dew-point:

| CHEMICALLY COMBINED WATER. | | | |
|----------------------------|----------|----------|----------|
| | 2½% | 5% | 10% |
| Tension of vapors..... | 47.9 mm. | 66.9 mm. | 93.5 mm. |
| Dew point | 38°C. | 44°C. | 51°C. |

Let us see now what effect would be produced upon the relative moisture of the furnace-gas, and consequently upon its capacity to absorb and carry off vapor in watersmoking, by supplying air to the fuel in quantities outside the limits stated above, although the latter probably correspond most nearly to the conditions that actually exist in practical operations.

Suppose four times as much air is supplied to the fuel as is required theoretically to burn the coal, a case which might very well occur if defective apparatus is in use. The given amount of coal, 200 kg., and the thousand bricks would require $4 \times 1580 = 6320$ cbm. air.

The products of combustion will be as follows, including the vapors rising from the clay during the firing:

| CLAY WITH CHEMICALLY COMBINED WATER. | | | |
|--------------------------------------|----------------------|---------------------|---------------------|
| | (Schwarz- hütte). | (Siegere- dorf). | (Greppin Works). |
| | 2½% | 5% | 10% |
| Nitrogen | 4993.6 cbm. | 4993.6 cbm. | 4993.6 cbm. |
| Carbon dioxide | 288.6 cbm. | 288.6 cbm. | 288.6 cbm. |
| Vapor | 209.0 cbm. | 302.1 cbm. | 488.3 cbm. |
| Oxygen | 995.4 cbm. | 995.4 cbm. | 995.4 cbm. |
| | <hr/> | <hr/> | <hr/> |
| Total | 6486.6 cbm. | 6579.7 cbm. | 6765.9 cbm. |

Therefore the vapor contained in the furnace-gas, expressed in percentages, is: 3.1; 4.6; 7.2; and the dew point: 26°C.; 32°C.; 41°C.

Suppose, on the other hand, the quantity of air supplied is not sufficient to reduce all the coal to steam and carbon-dioxide, but is sufficient to convert, we will say, the hydrogen and half the carbon into carbon dioxide, the other half of the carbon being merely reduced to a lower stage of oxidation, carbon monoxide,* and lost in the furnace-gas which escapes. In this case the analysis of the gas results as follows:

CLAY WITH CHEMICALLY COMBINED WATER.

| | 2½ % | 5% | 10% |
|-----------------------|------------|------------|------------|
| Nitrogen | 953.2 cbm. | 953.2 cbm. | 953.2 cbm. |
| Carbon dioxide | 144.3 cbm. | 144.3 cbm. | 144.3 cbm. |
| Vapor | 209.0 cbm. | 302.1 cbm. | 488.2 cbm. |
| Carbon monoxide | 144.0 cbm. | 144.3 cbm. | 144.3 cbm. |

1450.8 cbm. 1543.9 cbm. 1730.0 cbm.

In this case the percentages of vapor in the furnace-gases are: 14.4 per cent; 19.6 per cent; 28.2 per cent; and the dew-points are respectively: 54°C.; 61°C.; 69°C.

In all these cases the absolute amount of vapor in the furnace-gas remains unchanged, since it is composed of constant factors, namely, the water formed in the combustion of 200 kg. of coal,

| | Clay Containing Chemically Combined Water. | | | | | |
|---------------------------------|--|----------|--------------------------|----------|-------------------------------|----------|
| | (Schwarz- hütte). 2½ % | | (Siegers- dorf) 5% | | (Greppin Brick Wks) 10% | |
| | Humidity | Dewpoint | Humidity | Dewpoint | Humidity | Dewpoint |
| With insufficient supply of air | 14.4% | 54°C. | 19.6% | 61°C. | 28.2% | 69°C. |
| “ sufficient “ “ “ | 12.0% | 50°C. | 16.5% | 57°C. | 21.9% | 63°C. |
| “ double “ “ “ | 6.3% | 38°C. | 8.8% | 44°C. | 12.3% | 51°C. |
| “ fourfold “ “ “ | 3.1% | 26°C. | 4.6% | 32°C. | 7.2% | 41°C. |

*In perfect combustion 6 parts by weight of carbon unite with 16 parts by weight of oxygen to form carbon dioxide; if, however, the combustion is imperfect and only carbon monoxide is formed, only half as much oxygen, i. e., 8 parts by weight are combined with the same amount of carbon.

and the water expelled from 1,000 brick during the firing. The other constituents, however, vary greatly, both qualitatively and quantitatively, according as the air supplied for combustion is insufficient for complete combustion, just sufficient, or in excess.

Let us compare once more the figures given above in order to deduce from them general principles which will be of value in practical operations. When 200 kg. of coal are consumed in burning 1,000 bricks, the analysis of the gases is as in the last table.

From these figures it will be seen that, with the same clay and the same amount of fuel, the relative amount of vapor in the furnace-gas increases as the amount of air used for combustion decreases, and when the same amount of air is supplied, it increases as the percentage of chemically combined water in the clay increases. The dew-point of the furnace-gas increases also in proportion as the humidity increases.

This last fact is of importance, because the dew-point is the lowest temperature at which the furnace-gas can be used in water-smoking.

If the whole charge of the kiln has a higher temperature than the dew-point of the furnace-gases, the latter will be able to drive off the vapors; but if this temperature is lower than the dew-point, the bricks will absorb moisture and the result will be a more or less harmful effect upon the surface colorings, according to the temperature of the air, its percentage of moisture, the kind and amount of the saline or acid vapors volatized with the furnace-gas, the degree of porosity, and the percentage of salt which may perhaps be present in the clay.

But the absolute amount of air and its relative proportion to the amount of fuel which have just been discussed are not the only factors which have a decided influence upon the humidity of the furnace-gas. The absolute amount of fuel consumed must also be taken into account, since the fuel contributes to the formation of vapor and the amount of air used depends upon the amount of fuel.

The amount of fuel used may vary greatly according to the degree of hardness aimed at in the burning, and the temperature to which the wares must be exposed in order to attain this result.

Suppose we modify the case assumed above, first by reducing the quantity of fuel used for 1,000 bricks to 100 kg., then by increasing it to 300 kg. The composition of the furnace-gases is as follows:

1a. The quantity of air supplied is just sufficient for combustion, and 100 kg. coal are used for 1,000 bricks.

CLAY CONTAINING CHEMICALLY COMBINED WATER.

| | 2½ % | 5% | 10% |
|----------------------|------------------|-------------------|-------------------|
| Nitrogen | 624.1 cbm. | 624.1 cbm. | 624.1 cbm. |
| Carbon dioxide | 144.3 cbm. | 144.3 cbm. | 144.3 cbm. |
| Vapor | 151.0 cbm. | 244.1 cbm. | 430.3 cbm. |
| | <hr/> 914.4 cbm. | <hr/> 1012.1 cbm. | <hr/> 1198.7 cbm. |

The respective percentages of vapor are in this case as follows: 16.4 per cent; 24.1 per cent; 35.9 per cent. The dew-points of the furnace-gas are respectively: 57°C.; 65°C.; 74°C.

1b. The quantity of air supplied is twice as great as is needed theoretically for combustion, when 100 kg. coal are used with 1,000 bricks.

CLAY CONTAINING CHEMICALLY COMBINED WATER.

| | 2½ % | 5% | 10% |
|----------------------|-------------------|-------------------|-------------------|
| Nitrogen | 1248.2 cbm. | 1248.2 cbm. | 1248.2 cbm. |
| Carbon dioxide | 144.3 cbm. | 144.3 cbm. | 144.3 cbm. |
| Vapor | 151.0 cbm. | 244.1 cbm. | 430.3 cbm. |
| Oxygen | 165.9 cbm. | 165.9 cbm. | 165.9 cbm. |
| | <hr/> 1709.4 cbm. | <hr/> 1802.7 cbm. | <hr/> 1988.9 cbm. |

The respective percentages of vapor: 8.8 per cent; 15.5 per cent; 21.6 per cent. The dew-point: 44°C.; 55°C.; 63°C.

2a. The amount of air supplied is just sufficient for combustion; 300 kg. coal are used for 1,000 bricks.

CLAY CONTAINING CHEMICALLY COMBINED WATER.

| | 2½ % | 5% | 10% |
|----------------------|-------------------|-------------------|-------------------|
| Nitrogen | 1872.3 cbm. | 1872.3 cbm. | 1872.3 cbm. |
| Carbon dioxide | 432.9 cbm. | 432.9 cbm. | 432.9 cbm. |
| Vapor | 266.9 cbm. | 360.0 cbm. | 546.2 cbm. |
| | <hr/> 2572.1 cbm. | <hr/> 2665.2 cbm. | <hr/> 2851.4 cbm. |

The percentages of vapor in the furnace-gas are in this case: 10.4 per cent; 13.9 per cent; 19.1 per cent; and the dew-points: 48°C.; 53°C.; 60°C.;

2b. The quantity of air supplied is twice as great as is needed theoretically for the combustion of 300 kg. coal.

CLAY CONTAINING CHEMICALLY COMBINED WATER.

| | 2½ % | 5 % | 10 % |
|----------------------|-------------------|-------------------|-------------------|
| Nitrogen | 3744.6 cbm. | 3744.6 cbm. | 3744.6 cbm. |
| Carbon dioxide | 432.9 cbm. | 432.9 cbm. | 432.9 cbm. |
| Vapor | 266.9 cbm. | 360.0 cbm. | 546.0 cbm. |
| Oxygen | 497.2 cbm. | 497.2 cbm. | 497.2 cbm. |
| | <hr/> 4941.6 cbm. | <hr/> 5034.7 cbm. | <hr/> 5220.9 cbm. |

The amount of vapor expressed in percentages: 5.3 per cent; 7.1 per cent; 10.5 per cent. The dew-point: 35°C.; 40°C.; and 48°C.

The following table presents the dew-points calculated for the above mentioned conditions:

Consumption of Coal.

100 kg. 200 kg. 300 kg.

Quantity of air just sufficient.

Clay containing chemically combined

| | | | | |
|-------------|------|-------|-------|-------|
| Water | 2½ % | 57°C. | 50°C. | 48°C. |
| " | 5 % | 65°C. | 57°C. | 53°C. |
| " | 10 % | 74°C. | 63°C. | 60°C. |

Quantity of air twice as great as is needed.

Clay containing chemically combined

| | | | | |
|-------------|------|-------|-------|-------|
| Water | 2½ % | 44°C. | 38°C. | 35°C. |
| " | 5 % | 55°C. | 44°C. | 40°C. |
| " | 10 % | 63°C. | 51°C. | 48°C. |

From this table a law may be formulated as follows: The percentage of vapor, and consequently the dew-point of the furnace-gases, decreases in proportion as the amount of fuel is increased (other conditions being the same); or in other words, the harder the bricks are to be burned in the kiln, or the greater the amount of heat required to burn the material thoroughly, so much greater will the percentage of vapor be in the furnace-gas.

II.—The Amount of Air and Heat Needed for Watersmoking.

It has been shown: first, that the capacity of the furnace-gas to give off heat for the watersmoking process is diminished in proportion as its humidity is increased; and, secondly, that the amount of heat which must be obtained from some other source than the furnace-gases, in order to heat the newly-set bricks to

a temperature above the dew-point and then watersmoke them, is greater in proportion as the dew-point is higher.

Therefore those factors which have the effect of increasing the humidity of the furnace-gases will always have a tendency to lessen the chances of perfect success in the watersmoking process.

We have found that a large percentage of chemically combined water, and the combustion of coal with scanty supply of air are unfavorable factors of this nature. The latter factor, however, is one particularly calculated to secure the utmost economy in the use of fuel, provided the supply of air is not reduced below a certain necessary minimum.

Now that relation between fuel and combustion-gases which insures the greatest amount of heat can be more easily maintained when gas is used in firing, than when solid fuel is used, especially if the latter presents comparatively little surface to the contact of the air, and the economical use of fuel will always be the chief aim in view. Consequently the danger of producing harmful effects in watersmoking by means of furnace-gases will always be greater with gas-firing than in the annular kiln. In other words: under like conditions, greater precaution must be taken with gas firing, to prevent the condensation of the furnace-gases before their entrance into the flue, than in the ordinary annular kiln.

Let us assume average conditions for the operation of the annular kiln: for example, a consumption of 200 kg. coal; 5 per cent chemically combined water in the brick clay; and a supply of air twice as great as is theoretically required for combustion. From the tables given we shall obtain an average of 44°C. for the dew-point of the furnace-gases, that is, the temperature at which they are able to carry off in the form of steam, without precipitation of water in the form of mist or sweat, all the aqueous vapor formed during the firing from the coal and the brick material.

If the conditions under which furnace-gas is used for watersmoking are more favorable, the dew-point may sink to 26°C., or if they are less favorable, it may rise to 74°C. Therefore the bricks must be raised to this temperature by some other source of heat before they can be heated and thoroughly dried by means of the hot escaping furnace-gases, because otherwise the cold bricks coming in contact with the furnace-gas might cool the latter below the dew-point, and thereby cause aqueous precipitations in the chambers filled with green wares.

However, in order to avoid misunderstanding, I wish to repeat here that harmful results do not necessarily appear when water is

precipitated, but they are liable to appear under unfavorable conditions.

Water can be absorbed in the pores of air-dried clay (more in some kinds of clay than in others) without making the outer surface wet and consequently liable to attract flue-dust and other impurities in the furnace-gases; but if acid vapors are present in the furnace-gas, these penetrate into the pores of the clay together with the aqueous vapors and may then have an injurious effect upon the coloring. However, such an injurious effect will not be produced, or at least not to any great extent, if the aqueous vapor is allowed to escape from the pores of the bricks immediately after they come in contact with the hot furnace-gas. This will be the case when they have previously been heated to the dew-point of the furnace-gas in such a way as to prevent their suffering from it, that is, by special fires, which permit the access of sufficient air to carry off easily all aqueous vapors formed in this heating. This result is secured in the watersmoking fires in periodic kilns, and generally in continuous kilns, by supplying warm air through a smoke-flue.

If we say that 40°C . is the average temperature to which the bricks in the annular kiln must be raised, in order to bear the contact with the furnace-gas without injury, and 15°C . the temperature at which they are set in the kiln, then in the preliminary heating the temperature must be raised 25° , or in round numbers 30°C .

This heating is accomplished mainly by two factors: the heat radiating from the walls and floor of the kiln, and, if this is not sufficient, the heat secured by separate fires in the wicket doors, by special smoke canals above the fire holes, or by the introduction of warm air conducted from the cooling chambers of the kiln through smoke-flues.

Before passing to statistics on the quantity of heat required for this purpose and on the volume of air necessary to carry the heat and carry off the vapors simultaneously formed, it seems necessary, in order to make the subject perfectly clear, to present some principles and laws of heat with which the practical manufacturer is not always familiar.

It is known to everyone, of course, that temperatures are measured by the thermometer and (the higher degrees) by the pyrometer; we shall assume that the construction of these instruments is understood and also the principles upon which the scales are arranged and graduated.

These instruments are designed to indicate merely the inten-

sity of the heat, and do not give as yet any standard for the amount of heat which has been developed from any definite source of heat or collected in a definite heated mass. An illustration will make this plainer.

Imagine a certain source of heat as a gas flame or an alcohol lamp used to heat a dish filled with water, adjusted so that all the heat derived from the flame can be conducted into the water, all waste being avoided. Suppose the dish which is to be warmed contains 10 kg. water and the flame beneath it is able, in one hour, to heat these 10 kilograms of water from $0^{\circ}\text{C}.$ to the boiling point, that is, $100^{\circ}\text{C}.$

It can be shown now by experiment that, if the dish contained twice as much water at $0^{\circ}\text{C}.$, it could be heated only to $50^{\circ}\text{C}.$ in the same length of time, and 100 kg. water could be heated only to $10^{\circ}\text{C}.$

But in all these cases, assuming that the flame remains unchanged, the same amount of heat has been evolved and transmitted to the water although the thermometer has not registered the same number of degrees. Therefore we see that the amount of heat evolved is expressed not merely by the increase in temperature indicated by the thermometer but also by the amount of heated water, since the degree of temperature multiplied by the number of kilograms of water gives the same result in each case.

In order to combine these two factors, the temperature and quantity of the heated substance, in a single expression for the measurement of the heat proceeding from any source of heat, it has been agreed to take as the unit in measurements of heat the amount of heat absorbed by 1 kilogram of water while its temperature is being raised from 0° to $1^{\circ}\text{C}.$

This amount of heat is called a thermal unit or calorie. In the illustration given therefore the amount of heat evolved from the gas or alcohol flame would be expressed as follows: 10 kg. \times $100^{\circ}\text{C}.$, or 20 kg. \times $50^{\circ}\text{C}.$, or 100 kg. \times $10^{\circ}\text{C}.$ = 1000 thermal units.

It is evident from the foregoing explanation that if 1 kg. of water at $0^{\circ}\text{C}.$ is mixed with 1 kg. water at $100^{\circ}\text{C}.$ the result will be 2 kg. water at $50^{\circ}\text{C}.$ The case is different, however, when substances of different kinds are mixed together and the temperatures allowed to become equalized. If 1 kg. water at $100^{\circ}\text{C}.$ is mixed with 1 kg. mercury at 0° , the temperature of the mixture is not 50° but $98.8^{\circ}\text{C}.$ This is due to the fact that equal weights of all substances do not require the same amount of heat to raise their temperature $1^{\circ}\text{C}.$, and that much less heat is absorbed by 1 kg. of mercury than by 1 kg. water.

Starting from water, which of all known substances requires the most heat to raise its temperature 1°C. , and taking this as a unit, it has been demonstrated by very delicate experiments how much heat is required in the case of many substances to heat 1 kilogram 1°C. The number thus determined is in each case the specific heat of the substance.

The specific heat of the substances with which we are concerned in this discussion is expressed by the following figures:*

| | |
|---|--------|
| Water | 1.0000 |
| Atmospheric air | .2669 |
| Oxygen | .2361 |
| Nitrogen | .2754 |
| Carbon monoxide | .2884 |
| Carbon dioxide | .2210 |
| Aqueous vapor | .3010 |
| Burned clay (the mean average of three different varieties) | .2083 |

That is: 1.0000 thermal unit is required to raise the temperature of 1 kg. water 1°C. , .2083 thermal unit is required to raise the temperature of 1 kg. of burned clay 1°C. and .2669 to raise the temperature of 1 kg. of atmospheric air 1°C.

The above data enable us to calculate the amount of heat required to increase the temperature of any given weight of a substance by a certain number of degrees, or to find the amount of heat lost by any substance in cooling a certain number of degrees. In order to express this amount of heat in thermal units it is only necessary to multiply the weight (expressed in kilograms) by the difference in temperature, expressed in degrees Celsius, and the specific heat.

One cubic meter of air weighs 1.299 kg, at 0° and 760 mm. barometric height. To heat a cubic meter of air 100°C. therefore, $1.299 \times 100 \times .2669 = 34.56$ heat units are required, or as much heat as is required to heat 34.56 kg. water 1°C. , or 1 kg. water 34.56°C.

In order to heat a brick weighing 3 kg. 100°C. $3 \times 100 \times .2083 = 62.49$ heat units are required.

An unburned brick containing 3 kg. clay (burned), 5 per cent or 15 kg. chemically combined water, and 5 per cent hygroscopic water would require in order to be heated 100°C. ;

*Measurements of Schinz, Compendium of Heat (Compendium Warmemesskunst).

$3 \times 100 \times .2083 = 62.49$ heat units for the clay,
 $.3 \times 100 \times 1.000 = 30.00$ heat units for water contained in it.

Total.....92.49 heat units.

It is a well-known fact that when water is heated in an open dish, its temperature rises constantly until it reaches 100° C.; from this point on the thermometer shows no increase even if the supply of heat be increased, but all the additional heat is employed in changing the water from a liquid to a gaseous condition.

Our measurements have shown that, while 100 thermal units are required to heat 1 kg. water to 100° C., a much greater quantity is needed for evaporation—namely, nearly $5\frac{1}{2}$ times as much (540 thermal units), which is imperceptible to our senses and to the thermometer.

These 540 thermal units are called the latent heat of the vapor (hidden heat). There is required, therefore, all together $100 + 540 = 640$ thermal units to convert 1 kg. water at 0° C. into vapor at 100° C. On the other hand this latent heat appears again as free heat when the vapor is condensed, since 1 kg. of aqueous vapor when it is changed into liquid water, gives enough heat to raise the temperature of 540 kg. water 1° C., or of 5.4 kg. water from 0° to 100° C.

It has been found, furthermore, that if water is changed into vapor at a lower temperature than the boiling point, the quantity of latent heat remains unchanged and only the free heat shows a corresponding diminution. So if water is vaporized at 20° C., $20 + 540 = 560$ heat units are required for the formation of this vapor, or $50 + 540 = 590$ heat units are required to vaporize one kilogram of water at 50° C.

After this digression we will return to the application of the laws to a particular case. We had assumed that a brick clay contains, on an average, 5 per cent of chemically combined water, and that the temperature of the green bricks must be raised 30° C. before they can safely be brought into contact with the furnace gas of the kiln. Add to this another 5 per cent of water, which is retained in air-dried bricks, and the composition of 1,000 raw bricks will be as follows, assuming 3 kg. for the weight of each burned brick: 3,000 kg. clay (burned), 150 kg. chemically combined water, which is expelled only in the red heat, and 150 kg. water, which is to be removed by watersmoking, a total, therefore, of 3,300 kg.

The consumption of heat in raising the temperature of this amount of clay from 15° to 45° C. is as follows:

$3000 \times 30 \times .2083 = 18,747$ heat units for the clay,*
 $150 \times 30 \times 1.0000 = 4,500$ heat units for the chem. comb. water,
 $150 \times 30 \times 1.0000 = 4,500$ heat units for the hygroscopic water,
 $150 \times 540 = 81,000$ heat units for the latent heat of the vaporizing water.

Total.....108,747 heat units.

If this heat were generated by direct combustion—that is, by means of water-smoking fires, started at the wicket-doors, or by means of water-smoking kilns, the consumption of fuel used in producing this effect would be as follows; since it has been found that 1 kg. coal develops on an average 7487 thermal units, and 1 kg. wood 3878 thermal units during the combustion:
 $108,747 \div 7487 = 14.5$ kg. coal, or $108,747 \div 3878 = 28$ kg. air dried wood.

Suppose this heat is introduced by means of a smoke-flue, and that the temperature of the warm air entering the watersmoking chamber is 100° C. higher than that cooled by contact with the bricks, the temperature of the former being, for example, about 145° and the latter 45° C. As we have seen, one cubic meter of air requires 34.56 thermal units to be heated 100° C., and gives off the same amount on being cooled, so there would be required for a thousand bricks $108,747 \div 34.56 = 3147$ cbm. air.

The air used in this process is drawn in by suction through the open doors of the kiln under the influence of the chimney, passes through a part of the cooling chamber of the kiln, is here warmed and conducted through the smoke-canal to the watersmoking chamber. Suppose the temperature of the atmosphere without is 15° C., the temperature of the air employed in watersmoking would have to be increased $145^{\circ} - 15^{\circ} = 130^{\circ}$ C., and this heat must be obtained from the cooling bricks. One cubic meter of air weighs 1.299 kg.; therefore, the amount of heat transported by 3147 cbm., while the temperature is increased 130° , amounts to $3147 \times 1.299 \times .2669 \times 130 = 133,704$ thermal units.

Since the operation of the annular kiln must be considered as perfectly uniform, this quantity of heat required for heating and drying 1,000 bricks is to be derived from another thousand bricks standing in the cooling chambers, inasmuch as the latter give up their heat to the air utilized in watersmoking.

We have seen that one burned brick gives off or absorbs 62.49

*According to Person it would be more correct to take .474, the specific heat of the solid water or ice, but for the sake of simplicity I have taken that of the volatile water, since the final result is not altered essentially thereby.

thermal units when its temperature is lowered or raised 100° C. For 1,000 bricks and 1° C. 624.9 thermal units would be required, and the temperature of these 1,000 bricks would have to be reduced $133,704 \div 624.9 = 214^{\circ}$ C. by the current of air.

The result of this calculation shows that in order to raise the temperature of 1,000 bricks 30° C. by means of heated air and to vaporize the water contained in them, the temperature of another thousand bricks must be increased 214° C. in order to heat this current of air. This calculation represents the maximum consumption of fuel and it assumes that the walls of the chambers in which the bricks are set are completely cooled, so that no account need be taken of the heat radiating from them. As a matter of fact this is never the case in well-ordered operations, but on the other hand a very considerable amount of heat is furnished by this source for the preliminary heating. It is frequently found in practical operations that this heat alone is sufficient to preserve the freshly set bricks from injury by the furnace gas.

The amount of heat supplied by the walls depends not only upon the extent and nature of the surface from which radiation takes place, but also upon its temperature and upon the temperature of the substance which absorbs the radiated heat, in this instance the green bricks just put in.

The extent of wall surface of a kiln chamber does not stand in direct ratio to the capacity of the kiln, for the proportional size of the former increases as the latter is diminished. For example, the wall surface (including the floor) of a kiln of 10 cbm. capacity is 21.5 sq. meters, one of 30 cbm. capacity is 44.5 sq. m., and of 100 cbm. capacity 106.5 sq. meters. If we reckon 280 bricks to a capacity of one cbm., we find that in the first case mentioned there is a radiating wall surface of 7.7 sq. meters to a thousand bricks, in the second case 5.3 sq. meters, and in the third only 3.8 sq. meters. It is clear therefore that in smaller kilns the influence of the heated wall surfaces upon the newly set bricks is much greater and more favorable than in the large kilns.

In order to get a better understanding of the influence exerted by the heated walls, let us assume such conditions as are frequently found in practice.

The temperature of the newly set bricks is, we will say, 15° C. In the preliminary heating, before the access of the furnace gas, these bricks are to be heated to 45° C. and this preliminary heating must take place between two dampers, therefore, without circulation of air; the temperature of the walls, we will assume, is 60° C.; and we assume also that the heat radiating into the interior

of the chamber is constantly replenished from the sand masses of the thick walls of the kiln which are often red hot, so that the temperature of the walls remains constant at 60° C. during the 24 hours of preliminary heating.

According to the tables arranged by Schinz,* which were based upon experiments, we can calculate that under the above mentioned conditions of temperature one square foot (=0.09 sq. m.) gives off by radiation 43 thermal units in an hour (the standard of measurement being 1 lb. and 1° C.). This makes in 24 hours (calculated for square meters) 5735 thermal units (the standard being 1 kg. water and 1° C. as a thermal unit).

Accordingly in a kiln of 10 cbm. capacity the amount of heat radiated per thousand bricks would be: $7.7 \times 5735 = 44137$ thermal units; for a capacity of 30 cbm., $5.3 \times 5735 = 30375$ thermal units; for a capacity of 100 cbm. only $3.8 \times 5735 = 22804$ thermal units.

If, as is assumed in this case, there is no circulation of air during the preliminary heating, no vaporization of the water contained in the bricks can accompany the heating and there is no consumption of heat for vaporization in the form of latent heat. If we deduct the latent heat from the amount of heat calculated above for the heating of 1000 bricks to 45° C., there still remain 27747 thermal units, which are required to raise the temperature of the bricks 30° C. We see from this that the amount of heat radiated from the walls with a capacity of 10 cbm. is decidedly greater, and with a capacity of 30 cbm. is still sufficient to heat the charge from 15 to 45° C., and is inadequate to this purpose only when the dimensions of the kiln are very large.

If the heating and preliminary watersmoking are accompanied by the circulation of air, so that the air is at the same time the carrier of the heat supplied and of the vapors formed, the consumption of heat is much greater, on account of the additional latent heat of the evaporating water, than when the heating is accomplished by radiation from the walls alone; however in this instance the heat gained in the latter way is to be deducted from the total amount required. Thus if the water-smoking is to be performed by means of direct fires or air we shall obtain for a kiln of 10 cbm. capacity, 64010 thermal units; 30 cbm. capacity, 78362 thermal units; 100 cbm. capacity, 85933 thermal units, for 1000 bricks.

Calculating thus, the quantities of air still required to transport these quantities of heat, assuming that the temperature of the air is higher by 100° C. when it enters than when it departs, we

*Schinz—Compendium der Warmemesekunst. Tab. XLI and XLII.

shall get respectively 1852 cbm., 2264 cbm., and 2486 cbm. A comparison of these figures with those obtained in the calculation of the consumption of air in burning shows that in many cases the consumption of air is greater in the watersmoking process than in the burning process itself, provided that only perfectly air-dried bricks are introduced, and that care is always taken in the construction as well as the operation of the kiln to secure as thorough a circulation of air as possible in the watersmoking chambers.

This explains why the smoke canals and air passages, which were formerly constructed in small dimensions, were often inadequate, thus necessitating the employment of other appliances such as portable smoking furnaces. The smoke canals in the floor used in recent times in the Hoffmann kilns, which can be built in larger proportions than those used heretofore, are probably the only ones capable of accomplishing the transportation of the air and heat.

Let us suppose that in a fully charged kiln there are 280 green bricks to the cubic meter, and that .6 of the space is taken up by the bricks, .4 by the interstices between them, by canals and heating shafts; the space occupied by 1,000 bricks is found by calculation to be $1000 \div 280 = 3.57$ cbm., and the interstices between the bricks amount to 1.43 cbm.

We have seen above that for the removal of the given quantities of moisture the quantities of air which must be brought in contact with the bricks, and which are capable of giving off 100° C. heat, are respectively 1852, 2264, and 2486 cbm. Consequently the ventilation must be such that in the first case, in the 24×60 minutes, the air can be renewed $1852 \div (24 \times 60) = 1.28$ times a minute, in the second case $2468 \div (24 \times 60) = 1.72$ times. This may be looked upon as the minimum circulation, since it is rarely the case in actual practice that the bricks are perfectly air dried when they are put into the kiln. Now, in order to secure such a circulation, the kilns of older construction have plenty of cross sections in order to admit the air to the kiln and to let it escape when laden with vapors, since it is the rule here that in watersmoking all the fire holes as well as the smoke holes in the vault are to be entirely open.

In continuous kilns the same result must be aimed at. But it has already been practically demonstrated that no great success has been attained with little watersmoking fires at the wicket doors, especially in large kiln chambers and with smoke canals having few and narrow passages for the hot air. When materials

are used which are especially susceptible to discoloration on account of their physical and chemical nature, the result is scarcely worth mentioning.

But it has been made clear in the foregoing that even when there is a difference of 100° C. between the temperature of the warm air used for watersmoking and that of the escaping air, cooled and saturated with vapor, there must be a liberal use of means for securing ventilation within the kiln. These means are generally the chimney and smoke flues and it may be stated as a rule that the flue connecting the chamber which has been newly filled, and is to be preheated, with the smokestack is to be kept wide open during the watersmoking, even at the beginning.

If the warm air is taken from the cooling chambers, in which the temperature is not very high, there is no danger that the wares will be injured by too rapid heating since the dry air can carry very little heat. Besides it is possible at the outset to take the warm air from any part of the kiln where the temperature has already been reduced below 100° C., so that a slow heating is assured in any case.

If one examines from the standpoint of economy alone, the various methods employed in annular kilns for subjecting the bricks to a preliminary heating and drying, so that they may not be injured when brought into contact with the furnace gas, that method will appear unquestionably the best in which the sliding dampers are closed, the air excluded, and the bricks heated solely by the heat radiating from the walls to a temperature determined by the dew point of the furnace gas. And it has been shown that under favorable conditions, that is, with small kilns and well-regulated operation, this heat is quite adequate for the purpose. Of course the heat which is always absorbed by the walls of the kiln must be conserved as much as possible. Therefore the doors must not be pulled down too soon nor the fire-holes kept open, otherwise a great deal of heat will be wasted in the empty chambers of the kiln and in a part of those that are cooling off.

However, the circumstance must be taken into account that when the greatest possible conservation of heat in the kilns is practised, particularly in rather low kilns, the temperature of the chambers in which the workmen are engaged is often very high. Therefore, in order to keep the workmen in good humor, and also from sanitary considerations, many manufacturers forego the utmost economy of heat and so do not watersmoke at all, or give up trying to secure good coloring, which is always the most conven-

ient and the most foolish method of manufacturing, or else use extra fuel for a separate watersmoking.

More work is involved and consequently greater intelligence and careful supervision are demanded when a system of smoke-flues is employed, by which all the heat which escapes from the fire-holes, when the kiln is operated by workers who are not experts, can still be utilized without expense and successfully for preliminary heating, if the latter process is carried on to a sufficient extent.

The use of the smoke-canal presents another advantage which should not be underestimated—namely, the ventilation is much more vigorous in the chambers where the workmen are engaged than when the air required to feed the fire is drawn through the furnace. The workmen can, therefore, be very greatly relieved and no heat need be lost by opening the fire-holes.

It is not always possible to use this system, for several reasons: First, the plan of the kiln may be such as to render the construction of smoke canals impossible, or the kiln may be built on too small a scale to admit and control the large quantities of air which we have found to be necessary, or it may be impracticable on account of local conditions to put in subsequently such an apparatus, for it is always best to lay it beneath the floor of the furnace. In such cases recourse must be had to special fires for watersmoking, introduced either in the wicket doors, or, better still, above the fire-holes. These special fires demand, however, a greater amount of fuel and greater volume of air in order to secure as satisfactory results as are exhibited in the use of a smoke-flue constructed with suitable dimensions and properly operated.

Pottery Kilns with Gas Firing and Continuous Operation.

Under the above title an article appeared in the "Deutsche Bauzeitung," 1872, No. 16, written by Herr Mendheim, the engineer who constructed the new gas kiln in the Royal Porcelain Manufactory at Charlottenburg.

The writer of the article makes some comparisons between this gas kiln and the annular kiln with which I cannot altogether agree, and I therefore desire to continue the discussion, hoping to serve the interests of the pottery industry by bringing about a clear understanding of the subject.

It is beyond all dispute that the Hoffmann annular kiln, which has within a few years produced an epoch-making revolution in the pottery industry, especially in the manufacture of bricks, should be counted among the most important inventions of later

times, from the standpoint of national economy, and it is equally undisputed that the inventor of the kiln has gained a reputation extending far beyond the boundaries of his native land. In evidence of this we may point to the extensive introduction of the kiln into all branches of the pottery industry, about 800 being used at present, and to the fact that all the kilns used for pottery which have made their appearance in recent times and which aim at economy of fuel, are based more or less closely upon the fundamental plan of the Hoffmann kiln, that is, the continual advance of the fire in a closed ring, the greatest possible cooling of the escaping furnace gases and the utilization of the heat latent in the burned wares for the heating of the atmosphere in the kiln. There are, however, variations in the kind of fuel and in the design of the kiln chambers, according to the nature of the wares to be burned or the especial end to be accomplished. At first sight one would place this new annular gas kiln in the latter category.

The annular kiln has shared the fate of all great inventions. At first it was declared impractical and impossible by technical experts and non-technical workers. When, after unremitting study and great sacrifices, the inventor proved that in spite of the technical objections raised the kiln, when properly managed, would produce the best results, there arose immediately enthusiastic admirers on the one hand and on the other ignorant and envious men who made contemptible attacks upon him and endeavored, by taking advantage of a curious misunderstanding of the dispute on the part of the Prussian Patent Commission, not only to deprive him of the honor of the invention, but also to denounce him before the world as a most detestable plagiarist.

I do not class Herr Mendheim among these adversaries of the annular kiln. Herr Mendheim's investigations in connection with the erection of the new plant of the Royal Porcelain Factory are of unquestioned value for the pottery industry, and his views cannot be overlooked, as they have great weight, with manufacturers in this branch.

In the beginning of his article Herr Mendheim acknowledges the great advantages presented by the Hoffmann annular kiln in the manufacture of ordinary bricks, but declares that it cannot be used at all in the manufacture of finer products, such as high-grade pottery, facing bricks, even the better kinds of building bricks and clinkers, and he recommends that for the manufacture of such wares there be substituted for it *mutatis mutandis*, an annular kiln with gas firing on the principle of the Porcelain Manufactory at Charlottenburg.

Facts speak louder than theories, and in order to refute Herr Mendheim's statements I would only need to give here a long list of plants in which good building bricks and facing bricks are made in annular kilns. But I should like to go still farther and call his attention to the fact that even the world-renowned Oldenburg clinkers* are made in about half a dozen kilns, that the stoneware factories in Ziesar, Belgern, Gorke, Oberglauche and Krummnussbaum employ this system for glazed wares, that English factories secure with it a salt glaze on products from refractory clay, and that in one of the most important stoneware and faience factories in Lorraine an annular kiln is in the process of construction, in which the wares will be burned in saggars, since good results were obtained from experiments in another kiln. These facts to prove that after great economy in fuel has been secured it does not always seem necessary to relinquish it out of apprehension for the excellence of the products.

Of course all these factories have had to contend with great difficulties at the outset. That is to be expected in any plant. The same difficulties arose when the annular gas kiln was transferred from the manufacture of porcelain to that of bricks and they exist today in a great number of brickyards which cannot produce a single respectable backing brick. But if the manufacturer of finer wares, having acquired an understanding of the peculiarities of the kiln, has succeeded in overcoming the difficulties and in combining economy and excellence of product, it is reasonable to expect that when intelligence, which has heretofore been conspicuously lacking in workers in the ceramic industry, has once gained a foothold there, others with inferior wares will secure the same results. At any rate, just at this time, when the industry is beginning to revive, it does not seem justifiable to pass such a severe sentence as Herr Mendheim does.

The objection made in many quarters to the annular kiln, and the one especially emphasized by Herr Mendheim, is that it is said to be impossible to burn in the annular kiln products which ought to present a surface of uniform color, and that for this reason the advantages afforded by the system of continuous burning with direct firing must in many cases be relinquished in order to avoid the production of inferior wares.

In the case of glazed wares when fuel producing many ashes is used, this may be true, but it is by no means so conspicuous a drawback as Herr Mendheim imagines, for a prudent manufacturer will not use peat for the open burning of glazed ware

*F. Reisebriefe von Dr. H. Seger, Notizblatt, 1872, page 101.

in a kiln of any construction whatever, but a pure stone coal or wood. The objection is valid only in the frequently recurring case that the unreasonable demand is made of the annular kiln that it produce the finest products with the worst fuel that can be found. I think Herr Mendheim would be embarrassed even with the gas kiln, in the face of such demands, though perhaps not so much so as with the annular kiln.

All surface impurities in bricks which have been burned in an annular kiln are very unjustly attributed to the ashes, and although this may be true in the case of objects which come in direct contact with the fuel, it is certainly not the cause of all the discolorations, the latter being due for the most part to other sources. It is not difficult to demonstrate that the greater part of the discolorations of unglazed products are occasioned by the nature of the furnace-gases and the manner in which the heat produced is utilized to the utmost, and that the same phenomena must appear in the annular gas-kiln also, unless the same precautions are taken to prevent them as in the ordinary annular kiln. The neglect of these precautions will be avenged in a manner which Herr Mendheim considers to be some fault of the kiln.

When the fuel is converted into gas there is no longer the presence of ashes in the kiln chamber to contend with, but other much more serious drawbacks are not overcome; the chemical action of the flame is not altered, neither are the gaseous impurities of the combustion gases, which appear in all furnaces, removed, as these cannot, from very evident practical reasons, be purified.

Anyone who will take the trouble to examine the surfaces of bricks with magnifying-glass and microscope will be able to discern easily which impurities are caused by ashes and which are due to other causes. It will be seen that all deposits of ashes except those adhering directly to a clinker which has been brought to a vitreous fusion, which therefore, have in this case lost their form by fusion, can be easily recognized by their cellular structure, or, if the fuel used was stone coal, by the slaty, splintery or melted character, and can be removed more or less readily by rubbing or washing.

The observer will notice further that coatings which cannot be removed are most likely to appear on objects with a smooth dense surface, which is unfavorable to the adherence of ashes. This is especially true of machine made bricks and of the ordinary and facing bricks molded with water. It will be noticed also that they rarely or never appear on bricks molded in sand

with a rough surface. I beg Herr Mendheim to notice that marked deposits are frequently found upon the smooth surfaces of machine-made bricks, while they are entirely lacking or are much less marked on surfaces roughened by the wise cutter.

Even if these phenomena force one to further study, this much at least is certain, that they are not caused by ashes in the great majority of cases. Even the bricks from Flanders and the Lower Rhine, so inferior in form and durability, which are burned in meilers in direct contact with the fuel, do not exhibit such streaked discolorations, even when clinkers are accidentally formed, as are frequently found where more perfect firing-apparatus is in use.

This goes to show what an unimportant part is played by the ashes in the surface coloring of unglazed products. On the other hand there is evidence in kilns of any construction, in which discolored or cleanly burned bricks are standing, that the surfaces of the bricks may be covered with the finest flue dust without injury to their color.

Now even if it does seem bold to compare an apparatus which has demonstrated by a number of instances the possibility of securing good results with one which, so far as I know, has been constructed and operated in only one instance, there is all the more reason why we should wait for further evidence from the latter, since it has been used up to this time only in the production of the highest temperature attainable in technical science. However a well founded doubt may be allowed, as to whether the comparatively low temperatures in other branches of the clay industry may be extended with the same safety to the entire chamber of the kiln. It may well be questioned whether the same drawbacks of unequal heating which are peculiar to kilns of older construction will not appear here in greater degree.

Yet aside from these doubts, which can be dispelled or confirmed only by actual practice, it is not difficult to show that all the phenomena of discolorations must necessarily appear with gas firing which have been condemned in the Hoffmann annular kiln, in so far as the principle of the utmost utilization of heat is retained, and those precautions are disregarded which are necessary in operating the annular kiln as well.

In any case it must be admitted that the much more complicated gas kiln is more difficult to manage, so far as the maintenance and regulation of its functions are concerned, than the ordinary annular kiln, and yet the latter surely presents difficulties enough, and is a sufficiently severe test of the intelligence of the

workmen, as compared with the kilns which do not operate continuously.

If Herr Mendheim will inquire of the manufacturers of yellow bricks, whether any kind of fuel can be used in their manufacture, he will be told that the choice of fuel has a great influence upon the coloring in a kiln of any construction whatever, and that in this case it chances that the fuel producing the most ashes, such as peat and brown coal, if we exclude wood as a fuel altogether, is best adapted for the purpose, while stone coal rarely produces uniformly colored bricks but causes red discolorations on the exposed surfaces, which often extend to a depth of several millimeters into the clay mass.

Even if the red color alone did not exclude *a priori* the influence of the ashes, the depth of the colored stratum would surely do so, and the only remaining explanation of the phenomenon is the chemical action of the single ingredients of the furnace gas upon the clay.

Now chemistry teaches us that all strongly ferruginous clays, which at a certain stage of slagging assume a yellow or white color from the firing, must always contain an amount of calcium carbonate bearing a certain proportion to the iron, and that the red coloring of the brick which would otherwise be produced by the iron oxide is neutralized by the formation of a light colored iron-lime silicate.

If therefore the lime on the surface of the brick is used in any other way, so that it cannot enter into the above-mentioned light colored compound, the coloring power of the iron will appear in its full force. This case occurs frequently in practice and is always recognized by a red coloration when a stronger acid than the silicic acid is added to the lime during the firing, which may be done most easily at the beginning of the heating when water vapors can at the same time be condensed upon the surfaces of the bricks. Now sulphurous acid is always present in the furnace gases formed, when stone coal is used, and under the influence of the hydrogen and oxygen which are likewise always present in the objects to be burned, this acid converts the calcium carbonate on the surface into calcium sulphate (gypsum), and thereby renders the lime incapable of entering into a light-colored iron-lime silicate, or at least transfers this capacity to a higher temperature than is for other reasons practicable in the manufacture.

It must be remembered that gas is not a distinct kind of fuel with definite chemical properties. Its composition is dependent

primarily upon the nature of the fuel from which it is formed, and the difference in the chemical composition of the gas from stone coal, brown coal and peat can always be detected, since all the volatile elements of the solid fuel are contained in the gas, after the removal of all solid substances. Sulphur is one of these volatile substances besides carbon, hydrogen, oxygen and nitrogen, and consequently in all processes where sulphur can exert a harmful influence it will do so just as much when gas is used as when the corresponding fuel is used without being converted into gas.

There is one very essential difference between the kilns with continuous operation, including the annular gas kiln, and the kilns of older construction, inasmuch as in the former the heat once formed is utilized to the utmost and in its last stage is used for drying the wares just set into the kiln, while in the latter the furnace gases after a short circuit pass into the open air at a very high temperature, so that the drying or water smoking may be regarded as an independent process at the beginning of the firing.

This economical use of the waste heat however causes difficulties in the water smoking process, and this is something which cannot be avoided by changing the shape of the kiln, or by using any other fuel, even gas. Unless special precautionary measures are taken, there will be the same consequences in the gas kiln as those which appear in the Hoffmann annular kiln and in all those modeled after it, which, however, can in the latter case be remedied.

In the kilns of older construction the objects to be burned come into contact with a great volume of moderately heated dry air in the first stage of the firing—that is, in the water smoking, and in this air they easily lose their hygroscopic moisture; on the other hand in the kilns with continuous operation, the quantity of air is limited to the exact amount necessary to support the roasting fire, and moreover the air is not dry, but contains in the form of vapor a very considerable amount of water in chemical combination with the clay.

Now the cooling of the moist furnace gas can advance only to a certain limit without injuring the contents of the kiln. As the air is cooled more and more by contact with the bricks just put in and by the loss of the heat which is given up to form the compounds required by the ever-progressing vaporization, its point of saturation with vapors is soon reached or passed, so that eventually an occasional condensation of water must take place and this does take place under circumstances favorable

for it and results even in a partial softening of the bricks in the kiln.

If the greatest possible economy of fuel is the only thing to be regarded in the operation of the kiln, such an occasional condensation will be the rule in gas kilns as well as in all other annular kilns—that is, the cold bricks freshly set will perspire in the moist vapor-laden air of the water-smoking chamber and the consequences of this are familiar to every brickmaker; a firmly adhering whitish efflorescence appears upon the surface, and it is sufficiently clear from what has been said above, why this coating appears more rarely in the older kilns than in the annular kilns.

If we examine the nature of these efflorescences we shall not only discover the reasons why they are more apt to appear, as I said before, on the dense surfaces of facing bricks than on the rough surfaces of the commonest bricks molded in sand, but we shall also find the means to avoid them, unless, as frequently happens, they have been formed on the surfaces during the drying process, in which case they cannot of course be removed by the firing alone.

If the efflorescences just mentioned are examined with magnifying glasses they will appear as papillary, scaly, or vesicular masses, quite similar in appearance to those which are found upon air-dried and slightly burned bricks as well as upon very hard ones, and whose distinctive character disappears more and more when the base has passed into a clinker-like or partially fused state.

The chemical composition of these efflorescences has not often been determined up to this time, as it is difficult to obtain pure material in sufficient quantity. But the examination under the microscope shows that it is not an incrustation of ashes, since the latter can be definitely recognized, even if they are present in addition, but that it is a residue, crystalline in part, which was previously held in solution in the water, and when the water was vaporized was precipitated in solid form on the surfaces of the bricks, or else was extracted from the clay during the water-smoking process, when water was condensed upon the surface, and has been precipitated again upon the outside of the brick.

We shall not have to search long to find salts which can exert such an action and which are decomposed during the firing in such a way that the residue cannot be dissolved again in water. Carbonate of lime and gypsum are present in most clays in such quantities that the water which is contained in molded

bricks may be regarded as a saturated solution of these salts. Compounds of chlorine, especially common salt, are rarely absent. Pyrites is frequently an ingredient of the clay. It is weathered during the drying and together with the other insoluble ingredients causes the formation of ferrous sulphate, aluminum sulphate, and magnesium sulphate. Besides this, when water is absorbed from the furnace gas in the first stage of water smoking, ammonia salts, alkali salts, sulphurous acid, and sulphuric acid are condensed likewise, and unless such condensation is guarded against by precautionary measures, a considerable amount of soluble matter will be precipitated upon the surface of the bricks in the kiln.

When the water is vaporized, of course all the substances held in solution in it must be precipitated in solid form and the place where this occurs will depend entirely upon the character of the evaporating surface and upon the manner in which the water is removed. If the clay mass is dense and the drying is accomplished slowly, the vaporization of the water can at first take place only at the surface, but the liquid contained in the pores can be diffused toward the interior, and will exchange its greater proportion of salt from without for the lesser amount of salt of the inner liquid, until after further drying, the pores are opened and vaporization and final precipitation of the salts can take place within the clay mass also.

The leaner the clay, or the more porous the surface, the more readily this vaporization will take place in the clay, and therefore bricks with a rough surface exhibit these efflorescences less readily.

If, on the other hand, the vaporization is accomplished quickly, or if the pores are again filled with liquid, in this case by reason of condensation upon the surface, then the diffusion cannot take place in that short time, while the liquid and vapors are penetrating out from the interior, and all the substances held in solution in the water must be precipitated upon the surface and this will occur more easily, as the density of the surface is increased.

It will be seen, therefore, that the discolorations produced in this way, which make up the larger part of such phenomena, appear during the drying and watersmoking processes and have no connection at all with the real firing process. And unless the same more favorable conditions can be secured here as in the older kilns, the use of gas, even though it be purified, offers no protection.

In the annular kiln such measures have been partially adopted, and have been attended by excellent results, and the difficulties complained of at the outset have been overcome.

If Herr Mendheim had had time to study the English brick works, and if he had made himself familiar with the manufacture of facing bricks in Middle England, in Yorkshire, Chesheshire and Leicestershire, where annular kilns are in use, without any drying apparatus, where the bricks are molded from half-moist pulverized clay and are carted directly from the machine to the annular kiln, I scarcely think he would have been led to make the assertions which he does make in his article.

It is not my purpose to enter at this time into a detailed comparison of the Hoffmann annular kiln, and the annular gas kiln. The experience which has been gained with gas firing is still too little understood to justify one in pronouncing a verdict upon it. But this much I must say, that the use of gas for comparatively low degrees of heat calls forth very serious theoretical misgivings and actual practice alone will have to demonstrate how far these may be overcome.

Honor to whom honor is due. The annular kiln has certainly a great future before it in the manufacture of porcelain and the related branches of the ceramic art, and we have reason to be grateful to the Royal Porcelain Manufactory and to Herr Mendheim, who speaks in its behalf, for having opened the way for private industry. But the difference between the firing of porcelain, where everything is fused alike, and the manufacture of products with a porous structure, is very great, so that the experience gained here must be applied with the greatest caution to other branches of the clay industry. However, until further results are secured, the Hoffmann annular kiln will hold the place it has won, especially in the manufacture of bricks.

The Unsuccessful Attempt to Use Gas Firing in the Brickyard at Greppin.

In an earlier article, which appeared in the "Notizblatt," I have discussed the clay material used at Greppin. In that article I showed that the operation of a continuous kiln presents in itself greater difficulties in the securing of good colors in firing than the intermittent operation, and I called attention also to the fact that especial precautions, unnecessary in the older kilns, must be taken in order to prevent injury to the coloring of the surfaces through the mechanical or chemical action of the furnace gases.

I have chosen the clay at Greppin as an illustration on the present occasion also, because it is one of those clays on which the action of the furnace gases is more marked than is ordinarily the case with other clays.

I am willing to admit that if a Hoffmann annular kiln had been used instead of a Mendheim gas furnace, there would also have been difficulties to contend with at the outset, difficulties due, however, not to the system, but to local conditions, to peculiarities of the clay and the coal, which could have been obviated if the causes of the failure had been understood.

Frequent opportunity has been given for the discussion of the subject of gas firing in the meetings of our association during the last few years, and Mr. Mendheim and other gentlemen have reported on the success and the defects of the system.

In the use of gas for ceramic purposes a wrong method of procedure has been adopted from the very outset, in my opinion, because of the mistaken idea that an otherwise unsuitable fuel need only be converted into gas in order to obtain a pure flame which can no longer injure the color of the clay. This delusion has often been emphatically corrected in practical operations.

It seems to me altogether wrong to use the best kinds of fuel to produce generator gas for burning common bricks, facing bricks, terra cotta wares, lime and cement, yet in most cases manufacturers have been obliged to fall back upon the best fuel. It is wrong because there is no imperative necessity for using a complicated machine and a roundabout method, in which there is an inevitable waste of heat, to accomplish that which might be accomplished better and cheaper by a direct process.

When good coal is used, direct firing is unquestionably more economical than gas firing, in continuous as well as non-continuous kilns.

The wares exposed in the show room from the Siegersdorf factory bear witness to the fact that even the finer clay wares can, with careful treatment, be produced in the ordinary annular kiln. It is possible in this way to take advantage of the greater economy which can be secured with the annular kiln.

The chief advantage in gas firing in all branches of industry consists in the possibility of using an inferior kind of fuel which cannot furnish directly the requisite heat in the ordinary furnaces, either on account of its form or because it makes too many ashes or contains too much water or other impurities.

I shall, therefore, consider gas firing practicable for the firing

of ceramic wares only in those cases where local conditions make it necessary to use such inferior fuel, and where at the same time products of high commercial value are called for, as well as those in which flue-dust must necessarily be excluded on account of the high temperature required or on account of the glazed surfaces.

Difficulties have been encountered heretofore in the production of a stream of gas from such kinds of fuel sufficiently uniform for the firing, but I believe these difficulties have now been obviated by the use of the under-grate blast.

At first the action of the different constituents of the gas was not correctly understood, and it was supposed that if the ashes were done away with, all their harmful effects upon the coloring would be removed. But is the nature of the fuel changed when it is converted into gas? Does it not contain the same amount of steam, volatile sulphur compounds, ammonia salts, alkali vapors and perhaps other impurities, as when the poor fuel is burned on a grate? And are not these the very substances which produce the most injurious effects on account of their violent chemical action, for which reason they are more to be dreaded than ashes, and which distinguish the flame of fossil fuel from that of wood?

The chemical action of the flame, and especially the action of the volatile impurities, is exactly the same, whether the inferior and impure material is used directly or in the form of generator gas. In fact, it has been demonstrated in practical operation, and I have learned myself by experiments, that the action is more intense in the latter case, and it is my belief that thoroughly satisfactory results will not be obtained with gas firing, until it is possible to convert poor fuel into a gas from which harmful ingredients have been removed before its introduction into the kiln. I think the failure in Greppin as in other places is due to this cause.

The fuel which would doubtless be the most available for gas firing in North Germany is the earthy brown coal, or peat. I shall show by a little calculation the composition of the generator gas obtained from this coal. The water in peat fresh from the earth amounts to about 60 per cent of its weight. On exposure to the air the proportion of water decreases, but never goes below 25 per cent. At this point the coal is entirely powdery, but that which is usually called well-seasoned or dried, still contains on an average 40 per cent of hygroscopic water.

When this coal, containing 40 per cent of water, is converted

into gas under the conditions theoretically possible, i. e., when the carbon is burned to carbonic oxide with slight admission of air, the chemically combined hydrogen converted into volatile compounds and the free water vaporized, the result is a gas which contains besides nitrogen 26 per cent by volume of steam and only 25 per cent of combustible gases.

Mr. Mendheim has estimated the consumption of coal at 16½ hectoliters per thousand, so we can calculate how much steam will be added from the fuel to that formed during the firing from the clay as chemically combined, or hygroscopic water. In all branches of the pottery industry experience has taught us what harmful effects steam has upon the manufacture of wares either directly or indirectly.

Accepting Mr. Mendheim's estimate of the consumption of coal, namely, 16½ hl, and calculating 150 lb. of brown coal to the hectoliter, its heating capacity being assumed as one-third that of average mineral coal, we find that the consumption is about 896 lb. per thousand, a very slight saving, if any, compared with the old kiln.

There is no prospect of securing better colors with the gas furnace, and as a matter of fact, there is none when moist fuel is used, which is usually the case.

The problem to be solved, therefore, by gas firing, is not only the using of inferior fuel, but also the saving of fuel, and these objects cannot be accomplished in my opinion in the gas kilns constructed on the model of the Royal Porcelain Manufactory.

I am not opposed to gas firing as a matter of principle, but I am opposed to the Mendheim kilns in the brick industry, because I do not think they present any especial advantages over the older kilns, from the standpoint of economy.

The converting of the fuel into gas is of itself accompanied by a waste of heat, and we have discovered in other branches of industry that economy can only be secured with gas firing when the so-called regenerating process is connected with it, i. e., the heating of air and gas before they are united by means of the waste heat of the kiln. This process, however, is carried on to only a limited extent in the Mendheim kilns, for the air alone is heated here, not the gas. Besides, the construction of the kiln is such that a much greater amount of heat is stored up in the burned products and in the masonry than can be utilized in heating the air supplied to the fire, and it must, therefore, be allowed to escape into the open air.

In this respect the annular kiln offers much more favorable

conditions for the saving of fuel, since with equal production not more than half as much masonry has to be heated, and it is possible to heat in advance not only the air but also the gas. I consider it a problem worth the while of technical experts to study as to how gas firing may be substituted for the firing usually employed in annular kilns.

I am aware that attempts have been made in this direction for some time, but I think these experiments were not determinative since they were based upon false assumptions with reference to the movement and distribution of air in the kiln.

I have recently given much attention to this subject, as my interest was aroused by my investigations of furnace gases in annular kilns, and I am convinced that it is possible to construct the annular kiln so as to secure a uniform distribution of gas in the entire chamber of the kiln, the entire perpendicular section and consecutive compartments, and also a preliminary heating of the air and the gas before they unite with each other. In this way it would be possible to approximate more nearly the economy secured in the ordinary annular kiln than has heretofore been done in gas kilns.

On the Theory of Firing in the Annular Kiln.

An article appeared in the *Thonindustrie-Zeitung*, No. 51, 1877, on the firing of the annular kiln, in which the question is discussed, whether the annular kiln can be better fired by supplying all the feedholes at the same time, i. e., by putting in fuel at stated intervals, as the coal is consumed, every ten or fifteen minutes perhaps, or whether it is better to supply only one-third of the feed holes at once, putting in the fuel every five or eight minutes, and passing over two rows of holes each time. Referring to this article, W. Olschewsky gives in the "*Deutsche Töpfer-und Ziegler Zeitung*" a report of his investigations of the furnace gases with each of the methods described. I give below in tabular form the statements made in the article just referred to with reference to the composition of the furnace gases, which were taken at distances of one-half meter, one meter, and one and one-half meters beneath the top of the vaulted roof of the kiln, in the second chamber, during the preliminary fire, when all the feed holes were filled at intervals of 25 to 30 minutes:

| No. of test. | Depth below the arch at which the gas is taken. | COMPOSITION OF FURNACE GASES. | | | | Time after firing |
|--------------------|--|-------------------------------|---------|--------------------|-----------|-------------------------|
| | | Carbonic Acid. | Oxygen. | Carbonic Oxide. | Nitrogen. | |
| 1 | .50 | 12.2 | 8.2 | 0 | 79.6 | 1 |
| 2 | .50 | 9. | 11.2 | 0 | 79.8 | 5 |
| 3 | .50 | 5.6 | 14.9 | 0 | 79.5 | 11 |
| 4 | .50 | 4.6 | 15.7 | 0 | 79.7 | 23 |
| 5 | .50 | 11.4 | 8.9 | 0 | 79.7 | 2 |
| 6 | 1. | 8.8 | 11.6 | 0 | 79.6 | 5 |
| 7 | 1. | 5.3 | 15.1 | 0 | 79.6 | 13 |
| 8 | 1. | 12. | 8.9 | 0 | 79.1 | 1 |
| 9 | 1. | 9. | 11.4 | 0 | 79.6 | 5 |
| 10 | 1. | 5.2 | 15.2 | 0 | 79.6 | 10 |
| 11 | 1. | 5. | 15.6 | 0 | 79.4 | 16 |
| 12 | 1. | 3.6 | 17. | 0 | 79.4 | 31 |
| 13 | 1.5 | 10.5 | 9.8 | 0 | 79.7 | 2 |
| 14 | 1.5 | 5.4 | 14.9 | 0 | 79.7 | 7 |
| 15 | 1.5 | 4.2 | 16.2 | 0 | 79.6 | 12 |
| 16 | 1.5 | 4.6 | 15.7 | 0 | 79.7 | 22 |
| 17 | 1.5 | 4 | 16.2 | 0 | 79.8 | 28 |

A glance at the column giving the amounts of oxygen left in the furnace gases gives the best idea of the progress of the combustion.

Since the atmospheric air contains 21 per cent in volume of oxygen, and since each unit of oxygen produces one unit of carbonic acid in combustion, an approximate estimate can be made of the amount of unconsumed air which passes through the annular kiln.

Under the most favorable conditions; that is, immediately after all the feed holes have been fired, the percentage of unconsumed air is 39.1 per cent, nearly one-third, while it is 81.9 per cent, or over four-fifths, under the most unfavorable conditions, that is, after the fuel has been burned. The average of all the observations is 62.9 per cent, or roughly, two-thirds. In other words, in the case observed, there is, on an average three times as much atmospheric air passing through the kiln as is theoretically necessary for the most economical combustion.

This is not a favorable condition, yet it is, as a matter of fact, offset by other advantages. The heat from the cooling bricks and from the furnace gases which are passing off is utilized, so that the ultimate result is a great economy.

When each row of holes was fired at intervals of two or three minutes, the respective amounts of carbonic acid contained in the

furnace gases were 6.5, 6.9, 6.7, 6.9, 7 per cent, on an average 6.8 per cent, that is approximately the same as in the previous experiment, where the average was 7 per cent. So in this case also the amount of air passing through the kiln was three times as great as that theoretically required for combustion and the difference in the two cases is only that in the former case there is a variation of the mean value, as was to be expected.

As regards the pyrometric effect of the combustion, these two methods may be looked upon as in general equivalent, unless in the first case the variations in the composition of the furnace gases are so great, on account of the kind of fuel used, that the oxygen of the air disappears immediately after a plentiful supply of fuel has been put in, and unburned, combustible gases take its place. As I have said before, this case will occur the more frequently, the more easily and abundantly the volatile products of the fuel are formed, and the more readily the fuel burns with a flame.

As a result of his experiments Olschewsky concludes that the preference must be given to firing at short intervals, because, in the first method the temperature of the flame must vary greatly, as the composition of the furnace gases varies, and consequently fusion will occur easily when the temperature approaches the fusing point of the clay. Such a conclusion is, however, not justified, either in theory or in practical experience, and it is even opposed to that of the older periodic kilns, in which the variations in the nature and temperature of the flame must be much greater and of longer duration.

The increase in temperature can last only a few moments, as the table show, and can affect no more than the other surfaces of the bricks, while the center remains untouched.

If any great importance is to be attached to such an influence, but I do not think we are justified in doing this, it might have a favorable rather than an injurious effect upon the quality of the wares, since it would aid the slagging of the surface, while preserving the shape of the center, and this would be true in greater degree according to the increase of difference between the point of first softening and of the complete flux—points which are very remote from each other in some materials.

The practice of burning clinkers is also opposed to the theory of Herr Olschewsky, as this practice consists essentially in bringing the temperature of the bricks quickly to the fusing point of the clay by a vigorous fire and then burning off, allowing a slight decrease in the temperature to follow, in order not to put the resistance of the clay to too severe a test in the fire.

But even if it can be shown theoretically that firing at the short intervals of five minutes is to be preferred, yet there is another practical consideration which makes it difficult to carry out this plan; that is, the limited powers of the fireman, who cannot continuously watch the fire and feed it at intervals of five minutes.

The Firing of an Annular Kiln.

If we call to mind what direction is imparted to the air in the annular kiln, and how the fuel is introduced so as to correspond to the motion of the air, we shall see that it is a difficult matter to distribute the fuel so as to bring its surfaces at right angles to the current of the air.

The air is subjected here to the action of two forces, the upward motion of the heated air caused by its lesser specific gravity, and the horizontal motion caused by the action of the chimney.

The conditions for the movement of the air are very different in the different parts of the kiln, consequently first one and then the other of the forces acting upon it will gain the upper hand and determine its main direction.

The air always enters through the empty part of the kiln, passes through the tunnel of the kiln, meeting here objects which are intended to give up their heat in order to increase the temperature of the air.

Since the tunnel of the kiln generally has a higher temperature than the external air, the latter will, when it first enters, stay at the bottom, rising as it passes on and comes in contact with the wares in the kiln. When this upward movement is counterbalanced by the horizontal there will arise gradually an essentially horizontal movement in the parts of the kiln brought to a glow heat. Moreover the parts of the kiln where no more fuel is supplied to the moving air will begin to cool off. The resistance to the current due to the contact with the wares will become less and less the nearer the air approaches its outlet at the chimney. The farther it advances in this direction, the more it comes under the effect of the chimney and passes directly to it.

But a second process is going on in the remoter parts of the kiln. Here there are objects to be heated, which absorb a considerable amount of heat without becoming correspondingly hot themselves, since the heat is expended in forming water from the wares, and this water must be expelled from the kiln in the quickest possible way.

Suppose one of the remote chambers of the kiln is filled with moist bricks heated to 100° C. In expelling the water in the

form of steam five times as much heat is absorbed without increase of temperature, as was needed to heat the water to 100° C.

On account of the presence of this moisture the air must cool off very rapidly and will become more or less saturated with steam. But the cooled air, laden with moisture, is heavier than the warm, dry air and stays therefore in the lower part of the kiln, while the air which did not come in contact with the objects giving off steam fills the upper parts of the kiln. Consequently the distribution of heat in the last chambers is quite different from that in the one nearest to the fire.

Under the influence of the draft and the diminution of the friction of opposing objects, the gases pass down into the back part of the chamber which is being fired, so here the heat advances most rapidly on the bottom of the kiln, but in the water-smoking chambers we find the highest temperature at the top. At first sight this is a startling phenomenon and the explanation is not apparent at once, but there is a perfectly good reason for it in the different effect produced by the escaping heat in the chambers already heated and in those where the heat still comes in contact with objects giving off steam.

If the fuel is thrown into the annular kiln through a shaft constructed so that the fuel does not fall at once to the bottom of the kiln, but is distributed evenly on the walls of the shaft, thus forming a perpendicular stoke-channel, it will be possible to secure a uniform mixture of air and combustible materials in all parts of the kiln. If, however, such a distribution is not provided for at the outset, the fuel will follow the law of gravity and fall in heaps on the lower parts of the kiln, and since the combustible gases formed from it move in essentially the same direction as the air, they will not mix with the latter to the desired extent. Consequently the heat on the bottom of the kiln will often be much more intense than was intended, while on the other hand the air can pass through the upper parts of the kiln without coming in contact with combustible gases. Here the air meets with no fuel or with no great amount of it, and the case which was discussed before may easily occur here, i. e., there may be a waste of heat in the upper regions on account of excess of air and in the lower regions on account of lack of it.

A uniform temperature can never be secured in all parts of the kiln, when the fire is applied horizontally, because the air must then, from the very nature of things, circulate in a horizontal direction. Only when care is taken to distribute the fuel throughout the whole depth of the kiln with a regularity corre-

sponding to the circulation of air in the whole cross section of the kiln will it be possible to secure everywhere the same conditions for combustion and consequently the best combustion. For this reason all the numerous kilns constructed in recent times in imitation of the annular kilns will be complete failures if these fundamental principles are disregarded.

But how is an even perpendicular distribution of the coal to be secured, since the natural tendency of coal is to fall to the floor? Theoretically it is clear that the coal should adhere to the perpendicular walls of the feed shaft, but there are technical difficulties in carrying this out, since the law of gravity must be overcome, and yet the fuel must be distributed in the kiln with the same uniformity with which the air passes through it. I have often taken pains to examine closely plants where good results were secured with the annular kiln and my theories have been confirmed, since I have invariably found that the fuel was more or less systematically distributed.

In most cases, however, especially where uneven burning was complained of, the trouble could be traced back to an uneven distribution of the coal, and in some places most absurd experiments were tried, without success, of course, whereas a little technical knowledge and a moderate amount of reflection would have suggested the correct procedure.

The most frequent fault in the operation of a kiln is that the air is allowed to pass through the upper part of the kiln without coming into sufficient contact with the fuel or combustible gases, and the consequence is that the lower parts are, as a rule, better fired.

In an annular kiln constructed on the principle I have suggested the firing could never be accomplished from below, but always from above, since the fuel must be evenly distributed above as well as below, and this, of course, can not be effected unless it is thrown in from above.

I have often taken pains to instruct those who were operating annular kilns, but it has been my experience that in nine cases out of ten the work has been continued in the old faulty method. This is without doubt the cause of the many failures in the operation of the annular kilns, especially when the kilns are operated by workmen who had always worked previously with the horizontal draft and who did not possess sufficient knowledge to adapt their experiences with the old kilns to the altered condition of the annular kiln. This does not testify to a very great amount of intelligence on the part of those engaged in ceramic industries.

If anyone is really anxious to learn how to secure the best possible results with his apparatus, I will point out the method which must be adopted if satisfactory manufacture is to be attained.

Look first at the way in which fuel is put into the kiln. In most cases the feed shafts are constructed with a straight channel running from the fire hole in the vault to the bottom of the kiln.

When coal is thrown into such a shaft some of it may adhere to the shaft here and there, but the greater part of it falls to the bottom.

The necessity of distributing the coal has been demonstrated in practical operations and has been recognized by intelligent brick makers, but the ordinary way of accomplishing it is either to fix up a so-called "cross" in several parts of the shaft, on which the fuel is caught and kept at a certain height in the shaft, or to put in bricks which can be knocked over when the parts beneath them are sufficiently fired, so that the bottom of the kiln is, as it were, gradually raised. The objection to the simple arrangement of the "crosses" is that they either do not work or they work too much. Either all the fuel falls through and only a small portion stays on them, or some accident causes the whole amount of fuel to stop at this point and remain piled up there.

The only way to secure a proper distribution of the fuel is to leave plenty of room for the fuel to fall, so that it cannot become blocked in the feed shaft, putting, however, one obstacle after another in the way of the falling coal, so that it cannot fall directly downward, but must spring from one step to another, only a little remaining upon each step, so that there is no danger of its piling up or becoming blocked. This can be done by putting under each feed hole a lath about 4 in. wide and $\frac{1}{2}$ in. thick, and building up the feed channel around this according to the shape of the fuel, but in alternate layers, on either side of the lath, pushing the bricks close up to it. In this way the feed shafts are not only uniformly built up so that the same conditions for the distribution and firing of the coal are present everywhere, but they are also wide enough to obviate all fear of blocking and yet do not permit the fuel to drop directly to the bottom. A glimpse of the bottom of the furnace can be secured through the crevice formed by removing the lath.

When coal or any other kind of fuel is thrown into such a feed shaft, it can never fall directly to the bottom, but must

strike the projecting bricks several times and be scattered in all directions.

In certain cases such an arrangement is not desirable, for example, when the object is to produce the highest possible temperature, in which case a very large quantity of fuel must be kept in the kiln. In such a case there will be danger, if too much coal is thrown in, that it will not burn as quickly as it should, as the fresh coal will roll over the glowing coals and choke them. This can be obviated by building up whole columns of fuel in the kiln, not, however, extending down to the bottom, for then the circulation of air in the lower channels would be impeded. It must be done by making the feed shaft quite narrow at some point toward the lower end and then widening it again below this point. This is especially necessary in burning lime and cement.

Then this shaft can be closed at its narrowest point by throwing in large pieces of coal and forming, as it were, pillars of fuel, yet it will be possible to thrust a rod in and let as much of the glowing coal fall through to the floor as is considered necessary to produce the requisite heat at this spot.

In view of the horizontal draft which prevails here, it is not at all necessary to let much fuel fall through to the floor, because the flame is always directed this way and is often much stronger than is desired, and also because in the part of the burning room nearest the outlet toward the chimney the action of the draft is always stronger than in other places since the flame is forced into the horizontal flues. Since, therefore, the flame always has a downward direction here, it is often not at all necessary to put coal directly on the floor of the kiln; indeed, the result of this would often be to hinder the circulation of air there.

The firing of the annular kiln has been called the simplest imaginable form of direct gas firing, but this is a mistake, for it has less in common with the latter than any form of grate firing.

All fuels are decomposed at first in burning into partly combustible gaseous products, steam, hydro-carbons, hydrogen and a residue of charcoal (wood-charcoal, turf-charcoal or coke).

In gas firing, when there is imperfect combustion, which occurs when little air is admitted, and when there is a high combustion stratum, when there is, therefore, an abundance of coal in a glowing condition, the coke in the first stage of its transformation into gas is converted further into carbonic oxide, and this is converted in another place into carbon dioxide.

In grate firing part of the coke is burned to carbonic oxide and part is completely changed at once to carbon dioxide, according

to the height of the stratum and the strength of the draft, while in the firing of the annular kiln the latter process alone is the rule, since here there are the most unfavorable conditions for the formation of carbonic oxide, the chief ingredient of generator gases; the coal is spread out in small quantities in a thin layer and air and coal do not come into sufficiently close contact, yet large quantities of air are present.

To be sure, there is an extremely rapid evolution of combustible gases immediately after the fire is started in an annular kiln, since the fuel is put in in small quantities and well scattered, the hearth not being noticeably cooled.

But when this process is completed the rapidity of the combustion decreases very much, and in spite of the hot air of the furnace, the residue of coke, which always forms 50 to 70 per cent of the weight, even when the coal contains much gas, burns very slowly. The reason for this is that its temperature is not materially higher than that of the other contents of the kiln, at least there is never such a red heat as there is on a grate even when cold air is supplied, for in the latter case there is a very vigorous combustion on account of the close contact of air and coal.

This slow combustion of the coke residue of the fuel, which is a surprise to every practical worker, especially in the stoke-hole rows, which are already "dying out," can be explained on the one hand by the fact that in spite of the vigorous firing the intensity of the heat does sometimes decrease in the annular kiln, indeed the fire may go out entirely and it happens not infrequently that unburned coal is left, sometimes in large quantities, and on the other hand by the fact that a large quantity of atmospheric oxygen is constantly passing through the kiln without having been used for combustion. This is the cause of the very rare phenomenon of colored smoke in the chimney of annular kilns.

As the air passes through the kiln, advancing from one feed-shaft to another, it is gradually deprived of its oxygen, yet never entirely, for it is only the volatile constituents of the fuel which burn readily. However, the residue of coke has no decided action, since it comes very slightly in contact with the air, and it cannot therefore take any of the oxygen from the air. This has been proved by direct experiments and if it can be demonstrated after the air has passed all the feed-shafts filled with coal, it is true to a still greater degree of the middle and back parts of the kiln.

I have made reports* on former occasions about the process of combustion in an annular kiln in which the conditions were especially favorable for complete combustion of the oxygen, inasmuch as large quantities of fuel were used at once contrary to the practice usually adopted, especially with brick wares. These were experiments with reference to the nature of combustion products in an annular lime-kiln.

It was shown on this occasion that the furnace gases coming from the annealing fire did not lose the greater part of their oxygen until just after fresh fuel had been added, and that the proportion of oxygen increased greatly during the burning, so that half or two-thirds of it passed through the kiln unconsumed, but no excess of combustible gases, carbonic oxide in particular, could be observed.

Further experiments in an annular brick-kiln showed that only one-quarter to one-third of the oxygen brought into the kiln was really used in combustion when there was a moderate draft, and only one-half when there was a weak draft and the fire had just been started, so that the flame in the kiln must always be designated as a strongly oxidizing one with the ordinary method of procedure.

The atmosphere of the kiln is still oxidizing, even when the draft is entirely shut off after the fuel has been thoroughly heated, since the coke contained in the kiln cannot take all the oxygen even from the feeble current of air which appears on the floor of the kiln under these circumstances, and goes backward again beneath the arched roof. Reducing gases can act only in immediate proximity to the feed shafts, directly after the fuel is thrown in, and only in a small space. The colorings from those in the other parts of the kiln, which usually appear only in the immediate proximity of the feed-shafts are due to such reducing action.

In all other kilns, especially those of more primitive construction, the combustible gases are sometimes in excess and at other times the oxygen, and this alternation causes temporarily a more or less vigorous smoking. But in the annular kiln the oxygen predominates as a rule, and it is only when the space is limited and the fuel burns with much flame that a reducing action is apparent.

While the usual method of firing the annular kiln is invaluable in securing smokeless combustion, and is also greatly superior

*"Untersuchungen der Feuer gases im Kalkringofen mit dem Orsat'schen Apparat." Notizblatt des Deutschen Vereins für Fabrikation von Ziegeln etc., Heft 4, 1875.

from an economical standpoint, it is much more difficult for this very reason to secure uniform colorings than in any other kiln.

Anyone who has read carefully the articles on the action of the separate ingredients of the furnace gas upon the clay and the color phenomena connected with it must understand what an important effect temporary reducing influences have upon the color. It is clear that when the fuel used contains sulphur, and sulphur is almost always present in both mineral coal and brown coal, it is just the reducing gases which counteract the evil effects of the sulphur compounds and remove the discolorations already produced. It is also evident that when light colored slightly ferruginous clays are used the reducing gases assist in preventing the appearance of the colors caused by free iron oxide.

In the annular kiln the reducing influences keep more in the background or at least appear only in the immediate vicinity of the feed shafts and therefore they show more decidedly than smoking kilns the discolorations caused by the presence of sulphur with an excess of oxygen, which is always present at the same time.

It seems then that the appearance of smoke in the kilns used in the pottery industry has a real justification and is in fact sometimes necessary to produce certain colors.

The technical difficulties connected with the use of the annular kiln in many branches of the pottery industry, especially in the manufacture of terra cotta wares, have now been explained, and now that the trouble has been discovered, it remains to find ways and means of utilizing the results of scientific experiments in practical operations.

If this can be done, the annular kiln will be more extensively used, as it should be on account of its economical superiority, and it can be used with greater safety than heretofore in the manufacture of products which require pure and uniform coloring.

The scientist or manufacturer who is interested in producing better wares in the annular kiln than the average wares turned out with the usual management of the kiln, must first find some explanation for the possible causes of the various color phenomena which have up to the present time presented so many difficulties in this kiln. This will require careful investigation, for there are many different factors to be taken into account, and not every one will be able to overcome the obstacles lying in the way of an intelligent appreciation of the situation without scientific aid.

This is a matter in which scientific training alone is often not sufficient, and practical experience alone can only grope its way

hesitatingly. It is only when the two are combined and the study of an experienced worker is carried on according to scientific principles that a true understanding of the matter can be reached.

As everything in nature is subject to fixed laws, and nothing is done by accident, so it is with the colorings of clay which are under consideration.

It will be necessary to understand clearly whether certain colorings are really due to the action of the fire in itself, or whether they are not rather to be referred to influences exercised during the drying or water-smoking process; it must be made clear whether discolorations are not produced either by the efflorescence of salts from the clay itself, by, eliquation from it, or by the deposit of flue-dust and water-smoke moisture; it will be necessary to know what colorings the clay assumes under the action of oxidizing or reducing gases at different temperatures, when sulphur compounds are present and absent, and what shades of coloring are due to condensation in slagging.

Then in deciding upon the kind of fuel to be used, the following points must be taken into consideration: whether it should contain sulphur or not; whether it should abound in gas and burn with a flame for a long time, or whether it should furnish little gas and produce a flame for a short time only; whether it can be used in a moist or dry condition; whether it is necessary to put the wares in in such a way that much or little fuel can be stored in the feed shafts; whether a brisk draft or a slow one should be used in firing; whether a smoking chimney is to be considered a fault or defect in the working of the kiln, etc.

But the properties of the clay are various, and it is impossible to give definite directions about the management of an annular kiln, where wares of superior quality are to be produced. I think it is a mistake to be controlled in this matter by definite directions and so-called practical experience, for this may prove to be altogether unpractical in some particular case.

I cannot therefore take up in detail all possible cases, for this would only confuse the reader. I shall therefore limit myself to showing the proper method of procedure in one concrete case, such a case as often happens in practical operations.

Mr. E. of H. built an annular kiln in 1875 in order to save fuel and thus be able to compete successfully with neighboring brick-yards where local conditions were more favorable.

After investigating the subject and making experimental burnings in other annular kilns he convinced himself that the wares

in question, facing and ornamental yellow brick, could be burned quite as well in the annular kiln as in the older kilns. The kiln was constructed and put in operation under the supervision of a so-called "instructor;" but the brick which were turned out of this kiln were not yellow; they shone in all colors, green, yellow and reddish brown. To be sure they were more compact and the firing was of more uniform hardness, but colors were displayed which had never appeared in the old arched kilns.

The first failure was excused on account of the newness of the kiln and the moisture, improvement was looked for, the water-smoking was carried out with great precision, but all to no purpose—the result was the same, the hope of improvement grew weaker and weaker, experiments were tried at random till no one knew what he was doing. One chamber finally furnished a few hundred brick of the desired color, another several thousand. It was supposed that the secret had been discovered, but further operations produced no result at all.

The fancy bricks in Gothic shapes were of course unfit for use, even in mason work, so there was nothing to do but to fire the old kilns as quickly as possible, in order to keep the contract. All the advice received availed nothing, the brickyard filled up with discarded bricks, the owner became more and more discouraged, the master brickmakers grew wiser with every day and the workmen grew lazier and more refractory, and to crown all, the competitors made malicious comments. Certainly many of my readers have become familiar with such a state of affairs in their own experience.

The phenomena which appeared showed beyond a doubt that the clayey marl was colored in this case by volatile sulphur compounds in an oxidizing fire. In the old arched kiln the clay had assumed a straw yellow or light green color, except the upper layers, which were decidedly red with a whitish coating on the covered spots. Black spots, due originally to the grains of iron pyrites, showed beyond a doubt the action of strongly reducing gas flames in the old kiln.

In the annular kiln even the hard burned bricks showed in their fracture not a yellow or yellowish green color, but reddish or brownish yellow; the surface of the parts exposed in the kiln had more or less red or reddish brown spots, the covered parts had the same color as the inner part of the brick, the grains of iron pyrites had come to the surface, not as slag spots, but formed a loose red powder of iron oxide, thus showing a constantly oxidizing fire. On the mistaken assumption that the smoke was the cause of the bright colors, the covers of the feed holes were

lifted in the preliminary fire in order to admit more air into the furnace and thus burn the smoke.

It was only in the immediate vicinity of the feed shafts, where the bricks came into direct contact with the coal, or where the tapping flame had struck through, that the bricks showed the straw yellow color desired and heretofore obtained.

An inspection of the phenomena observed in the annular kiln and the products of the old kiln could leave no doubt as to the method of procedure which should be adopted, based on the scientific principles which have been discussed in connection with the clayey marl of Birkenwerder. The cause of the reddish color of the clay was the lack of a reducing atmosphere in the kiln, which was even carefully avoided; the reddish brown flames were due to the same cause and also to the sulphurous acid coming from the fuel.

It seemed necessary in order to remedy both faults only to fill the kiln chamber temporarily with a very gaseous, that is, smoky atmosphere.

With this end in view all the smoke vents of the annular kiln were closed while the fire was nevertheless fed with coal and with even larger quantities of coal than usual.

The result was that the entire kiln was filled with thick black smoke which was allowed to escape through one or two rows of wood holes, during the latter part of the firing, if the glow still appeared decidedly red, in order to avoid a deposit of soot and the consequent blackening of the kiln chambers beginning to cool off.

With this method of procedure such a quantity of sulphurous acid escapes with the smoke that it is almost impossible to stay in the kiln, and an appropriate way of conducting these gases away, from sanitary considerations, is a problem yet to be solved.

Coal was thrown in again as soon as the atmosphere in the feed holes and chain holes began to clear again. After the smoke had been allowed to act from 45 minutes to one hour the kiln was operated as usual, but this performance was repeated at intervals of eight hours. The success was complete, as had been anticipated from the scientific premises.

The brick had the normal yellow color to the very center throughout the entire kiln, while heretofore this color had appeared only in the feed shafts. The reddish brown flames and spots disappeared and today the kiln turns out facing bricks just as good and as pure in color as those made in the old kiln, while the cost of burning has been greatly reduced and there is much less breakage.

The method adopted in this particular case is of course not to be recommended in all cases; yet, if the cause of the trouble is carefully looked into, other difficulties can frequently be overcome in just as simple a manner.

Carbonate of Lime as an Ingredient of Clay.

ITS INFLUENCE UPON THE PROPERTIES OF THE CLAY, ESPECIALLY WITH REFERENCE TO THE MANUFACTURE OF FACING BRICK.

Of all the admixtures contained in the ordinary potter's clay and brick clay, which were incorporated with it during the natural washing process to which the clay owes its origin, the one of most frequent occurrence and of the greatest importance in manufacture is carbonate of lime.

The clay which results from the action of the atmosphere and water upon non-calcareous rocks is of course free from lime in the beginning, but before it is deposited in strata it has many opportunities to become mixed with substances containing lime.

The clay deposits at the mouths of a system of rivers contain not only the pure clay mud carried by some of the rivers in their individual courses, but also the pulverized and weather-beaten products of calcareous rocks and limestone mountains brought by other rivers to the place of deposit.

Besides this, fresh waters as well as the ocean, contain shell fish and snails and billions of microscopic creatures of manifold variety, and their calcareous shells, which are formed from the calcareous salts held in solution in the water, fall to the earth, as one generation after another dies, and are mingled with the clay mud in rivers, swamps, lakes and seas, where they not only give the clay in some cases a large proportion of lime, but even form of themselves great deposits of pure carbonate of lime, such as fresh-water limestone or chalk.

The lime contained in the clay is usually found only to a slight extent in chemical combination with silicic acid and alumina. For the most part it is mechanically mixed with the clay in the form of carbonate of lime, the presence of which can easily be determined, even by one who is not an expert, by pouring over the clay an acid fluid such as sulphuric or hydrochloric acid or strong vinegar. A violent effervescence betrays the presence of calcium carbonate.

It is commonly supposed that the clays which effervesce when acid is poured over them, those which have therefore a considerable proportion of carbonate of lime, are unsuited for the manu-

facture of bricks, but this is by no means true in every case. Carbonate of lime is often a very desirable ingredient of the clay, if it is present in moderate quantity and in sufficiently pulverized condition, for it aids the slagging during the firing; but if it occurs in large solid pieces, as lumps of limestone or chalk, shells, spheroidal, spherical or columnar concretions (so-called "marl puppets"), such as are especially frequent in the upper strata of clay beds when the clay has cracked or when roots have crowded in and water runs into the channels thus formed, the clay containing these foreign ingredients is utterly unfit for the manufacture of any kind of bricks, unless it is washed, sometimes even when the particles of carbonate of lime are so small that the naked eye can scarcely detect them. But if the carbonate of lime contained in the clay is so finely pulverized that the tiny particles cannot be distinguished from the rest of the clay mass with the naked eye, and cannot be separated by washing, then it will generally have no detrimental effect upon the clay, unless it is present in very large quantities.

It should be understood, therefore, that when calcareous clay is mentioned in the present chapter, only that clay is meant in which the carbonate of lime is so finely pulverized that it cannot cause any cracking after the firing is completed. The utmost limit for the proportion of carbonate of lime in clay which is designed for weatherproof material may be set at 25 per cent, if the firing is thorough, although now and then some clays are used which contain 30 to 33 per cent. If the carbonate of lime exceeds this amount the burned products show a tendency to disintegrate from the action of the weather and to form so-called "saltpeter formations," which, however, betray their presence even when there is much less lime in the clay, if the temperature is not increased during the firing at least to the point where slagging begins.

Although there are other factors which play an important part, yet it may be said in general that those brick materials which contain a considerable amount of carbonate of lime are more susceptible to the action of the atmosphere than those which contain less, especially if the firing was not hard.

For this reason the red-burning clays, which contain little or no carbonate of lime, are preferred for the products most exposed to the weather, i. e., the roofing tiles, while the clays containing much carbonate of lime, which usually burn yellow, are quite unfit for this purpose.

This property of calcareous clays, that is their susceptibility in general to the action of the weather, is, however, partly offset

in practical operations by the fact that they do not possess a very high fusing point, and can therefore be brought easily to that degree of slagging which renders them sufficiently impervious to atmospheric attack.

Many of the clay beds in the North German lowlands and on the shores of the Baltic and North Seas contain as much as 20 or 25 per cent of carbonate of lime, and they have on that account many desirable properties, although as we shall see presently, the manufacture of bricks from this clay presents many difficulties on this very account.

Since the finely pulverized carbonate of lime is a non-plastic material, the clays which contain a large proportion of it originally, even those of fine grain, that is, those which have passed through either a natural or artificial washing, are usually not too plastic for use as brick material, and do not need therefore the addition of any ingredient to make them more meager. They usually absorb water easily and rarely show a decided so-called "water-stiffness." They require comparatively little water to make a paste sufficiently plastic to be worked, and consequently show only a slight shrinkage in drying and very little tendency to crack, all of which properties are due to the finely pulverized carbonate of lime.

Several years ago some experiments were made for the benefit of those members of the "Deutscher Verein für die Fabrikation von Ziegeln, etc.," who work their clay with machines, with the following result: The clays in question could usually be formed into a clay stream with water amounting to 20 to 24 per cent of the drying substance, while the less calcareous clays, the brown coal clays and ferruginous clays of later formation, usually required 28 to 35 per cent of water to form an equally plastic mass, and the latter showed a correspondingly greater shrinkage.

Since the calcareous clay loses in the firing not only the water chemically combined in it, but also the carbonic acid, which makes up about 44 per cent of the carbonate of lime contained in it, the products made from this clay are lighter and more porous, the greater the proportion of lime. They also exhibit very slight shrinkage up to the temperature at which liquefaction begins; from this point, however, the mass liquefies very rapidly and loses its shape, so that it is more difficult than with other kinds of clay to produce the sharp-cornered straight-edged clinker bricks, with a porcelain-like vitrification which, when they are once produced, prove remarkably impervious to the weather.

The clay does not "stand in fire," to use a technical term. Sci-

entifically expressed this would mean that the temperature at which softening begins, so that the pores are closed and a compact porcelain-like paste is formed, and that at which complete liquefaction to slag takes place are quite near to each other, so that in general much greater skill is required to avoid fusion, that is, to produce good straight sharp-edged clinkers, than is necessary in the manufacture of other brick materials which soften less rapidly.

This circumstance increases greatly the difficulty in the manufacture of weather-proof bricks from calcareous clay, and it is often necessary, in order to get the correct shape, to stop at temperatures at which the bricks may indeed obtain the characteristic yellow color, which indicates that the fusion of the lime with the other ingredients has taken place, but do not lose their highly porous earthy fracture.

Such products, which are often incorrectly called "facing-clinkers," form the greater part of the light-colored brick material used in North Germany for facade-facings, although the great porosity of this material makes it ill-adapted to this special purpose.

If the firing is not entirely perfect these bricks will present little resistance to the northern climate on account of the brittleness, which is characteristic of the calcareous paste. Moreover, they will soon assume an ugly gray or black color from the absorption of the water and dust and soot floating in the air or else they will turn yellowish-green or bluish-green from the luxuriant growth of little plants upon their surface, such as algae and microscopic fungi.

These evils can be avoided only by burning the wares so hard that the condensation is quite marked, yet this is not feasible in actual practice, when the clay contains much lime, at least for visible brick work, since this causes great diminution of volume and consequently a decided change in shape.

The various kinds of calcareous clay found in extensive deposits in the plains of North Germany are frequently spoken of as a material especially suitable for the manufacture of clinker bricks. This is done in the hope that this will result in a more extended use of clinker bricks, which are better adapted for visible brickwork in a northern climate. This seems reasonable on superficial observation, but on closer examination of the characteristics of this material, it will be seen that it is not due to the often censured lack of intelligence or of technical knowledge on the part of brickmakers, that clinkers or bricks resembling clinkers are not

coming into more general use for facades, but it is rather due to the fact that the material itself is of such a nature that it is extremely difficult, owing to very evident practical considerations, to increase the temperature in the firing more than is necessary to render the bricks just hard enough for transportation and building.

It is true that the lime contained in the clay affords an excellent means for the formation of vitreous compounds in the heat and these permeate the clay paste, as it were, and make it impervious to the action of the weather. But it must not be forgotten that the carbonate of lime furnishes the clay not only with the desired lime, but also with carbonic acid, and to overlook this fact is to betray a one-sided view of the subject, owing to which many practical experiments have already been frustrated.

Clays which are recognized as good material for clinkers, such as the products of Oldenburg and Schwarzhütte, which aroused the interest of all competent judges at the exposition of building materials at Berlin, lose from three to four per cent of their chemically combined water in the firing and thus interstices are left which, at a sufficiently high temperature, can be entirely filled, forming a dense brick paste without any appreciable change in volume. In this case it is the particles of easily fusible minerals which cause the cementing, while the lime on the other hand promotes first the formation of easily fusible silicates.

In the case of calcareous clays the loss of weight is much greater. In those which contain so much lime that they assume a yellow or later a green color, this loss of chemically combined water and carbonic acid is seldom less than twelve per cent of the dry weight and is frequently from sixteen to eighteen per cent. While these volatile substances do not at a moderate temperature cause any noticeable shrinkage, they do at first make the structure of the clay much looser, but when the clay is heated till it begins to soften, the interstices which remain when the volatile substances are expelled must be filled, and this will of course cause a corresponding reduction of volume. If therefore the firing temperature is to be increased to the point which will render the material impervious to all influences of the atmosphere, the clays containing much lime would undergo such a decided change of form and the practical difficulties would be so greatly increased, that this very circumstance would make it impossible to use this material for visible brick work.

If therefore really weather-proof products are to be manufactured from materials containing lime, the proportion of lime must

not exceed a certain limit on account of the great shrinkage in the fire. One can not make a mistake in assuming from twelve to fifteen per cent of carbonate of lime as an admissible maximum. This quantity is scarcely sufficient to produce the desired yellow or yellowish-green colored bricks, if the clay contains ~~much iron at the same time, but for the sake of securing this color, this~~ limit is often exceeded, to the great detriment of the products so far as capacity to resist the action of the atmosphere is concerned.

Another property of the carbonate of lime, which comes into consideration in the manufacture of facing bricks and terra cotta wares, has already been mentioned, namely, that it imparts a yellow or yellowish-green color to the ordinary brick clays. This color, as well as the ordinary red color of the clay, is due to the iron oxide, which is never absent.

When brick clay is free from lime, the iron oxide causes a red color, varying from pale to dark red according to the amount of the oxide and the degree of heat in the firing. If carbonate of lime is added to such a clay by a washing process, the clay will burn yellow, if there is a sufficient amount of the carbonate. Direct experiments have shown that this yellow color is still noticeable if the clay contains at least from three to three and one-half per cent of carbonate of lime to one per cent of iron oxide.

The yellow coloring appears at a lower temperature and is lighter, as the amount of carbonate of lime exceeds this minimum, but appears at a higher temperature and shades off into yellowish red or yellowish brown the nearer the amount of carbonate conforms to the proportion given above.

If there is a less amount of lime, it may indeed alter the red color of the clay, but a pure yellow color will not result from the firing, and intermediate shades will appear, objectionable, undecided colors, such as are seen in most of the ordinary bricks, which cannot be used for visible brick-work.

It is clear from what has been said above, that if the chief stress is laid upon pure colors in the manufacture of bricks, which is unfortunately too often the case, these can be secured easily only with those varieties of clay in which lime is altogether absent, or is present in such slight quantity that it cannot affect the red coloring of the iron oxide, or when there is a sufficient quantity to change the red color easily into yellow. The latter extreme frequently tempts the manufacturer to pay too little atten-

tion to the securing of the most perfectly weather-proof products, as has already been mentioned.

I have just said that the yellow color cannot easily be secured unless the clay contains the largest possible amount of lime, but I do not mean by that, that this same result cannot be secured to a certain degree, if especial precautions are taken, with the moderate amount of lime which I have spoken of as the most desirable in the manufacture of clinkers under the given circumstances. The discussion of this question, to which too little attention has been paid up to this time, I shall leave for a future occasion.

The Coloration of Bricks.

A very annoying feature in the manufacture of yellow-burning bricks is the appearance of red flames on the yellow bricks.

Two yellow bricks are lying before me, one from the brick-yard of Herr Hecht, in Neu-hof, near Stralsund, the other from Sczegedin, in Hungary. On the surface of each there is a red incrustation sufficiently pronounced to furnish material for analysis, by means of which the cause of its appearance can be determined. Samples of the crust and the yellow body of the brick were analyzed, and from the difference in the composition of the crust and the brick, the cause of their different color has been determined.

Before entering upon a detailed explanation of this phenomenon, I will review briefly the conditions which give rise to the colorations of burned clay.

The analyses of different kinds of clay include usually the same constituents: silicic acid, alumina, iron oxide, small quantities of manganese, lime, magnesia, potassium, sodium, sulphuric acid, carbonic acid, a slight amount of phosphoric acid, and water. The coloration of clay products is therefore due to these substances, unless it is produced artificially by the admixture of various metal oxides, such as oxide of chromium, uranium, manganese, or copper.

In the entire list of constituents native to the clay, the only one which can produce the manifold varieties of color in the burned clay products is iron oxide. The color ranges, as is well known, from white, yellow, orange, red, blue and brown, even to black, and in the greatest variety of shades, all these being due to the compounds of iron.

This may seem strange, for a certain cause usually produces a certain effect, and it sounds incredible to say that a single substance is the cause of such varied effects in color. Pure kaolins furnish an illustration of this; after the firing they show the white color so familiar to us in porcelain. Common bricks have a red color, but many of them exhibit a variety of shades of yellow.

In a former article I described the manufacture of the blue flag-stones of Holland and showed that their color is caused by iron.

In the last few days I have been examining a specimen of clay which comes from Ziesar and is used there as a glaze for refractory clay. This clay contains considerable iron and shows a red color when held over the Bunsen burner. When subjected to more intense heat, in the blast, until it melted, a blue color appeared. The glaze of the wares for which it is used is yellowish brown. It appears then that the same substance can produce a red, blue and yellow color.

To say that all these colors are produced by the same substance suggests the art of the magician, who pours first red and then white wine from the same bottle. But there is no arbitrary will at work here, and the chemist is right in saying that all these colors are produced by the compounds of iron.

Iron occurs in different stages of oxidation, namely, ferrous oxide, ferric oxide, and ferro-ferric oxide. Everyone has seen iron rust, which is a compound of ferric oxide with water.

Taking no account of the water, there are present in it 28 parts of iron to 12 parts by weight of oxygen.

Ferrous oxide is not so well known, since it is not often found in a native state. It contains 8 parts of oxygen to 28 parts of iron. Another compound is ferro-ferric oxide which contains 10 parts of oxygen to 28 parts of iron.

In combination with silicic acid, these different oxides form compounds of different color. Ferric oxide produces red and yellow, ferrous oxide, blue and green, while ferro-ferric oxide occupies an intermediate position. The greatest variety of mixed colors results from different mixtures.

So far as the other constituents of the clay are concerned, the manganese does, to be sure, produce a brown color, but as it occurs only in very small quantities in the clay together with iron, its influence upon the color may be ignored. Its effect is merely a slight alteration of the shade of color.

Of the remaining constituents of the clay, there is not a single one which can produce color independently. These substances play a part only in so far as they affect the action of the iron compounds. Lime, in particular, is capable of completely neutralizing the coloring power of iron. It is claimed that magnesia has the same effect, but satisfactory tests have not yet been made.

In this very matter, the explanation of the appearance of red flames on yellow bricks, an important part is played by the lime. It is well known that yellow-burning clay, when heated to the temperature required to expel the chemically combined water, assumes a red color. When the temperature is increased, the color changes from white to yellow and orange, until finally, in the clinker stage, the color is green.

The question arises now: how is it possible that the tendency of iron to produce a red color is neutralized by lime? We can only reply that no entirely satisfactory result has been reached by experiments. It is the opinion of Prof. Remelé that a double silicate of iron with lime is colorless. But it might also be assumed that another compound is formed in this yellow clay, bearing some analogy to the coloring principle of the cement. The experiments of Dr. Michaelis show that it is probable, if not positively proven, that the coloring matter in Portland cement is calcic ferric oxide. This compound is olive green. If the heat in the kiln is sufficient to set the lime in action, this compound can easily be formed.

In answer to the question, how is it possible that an intermediate stage of white occurs in a green-coloring compound, the following explanation may be accepted. It is seen that the red color gradually fades and passes into green. Green and pink, it must be remembered, are complementary colors, i. e., their union produces white. Therefore it is evident that the transition stage is white, and that the green color is not marked until all the lime is made active under intenser heat, and the last trace of pink has disappeared, leaving only the green color of the calcic ferric oxide.

Although a definite statement cannot now be made about this matter, yet this much is certain, that there must be a definite percentage of lime in the clay in order to neutralize the coloring power of a definite amount of iron oxide. It may be said that when there is from 4 to 5 per cent of iron oxide present in the clay, about 10 per cent of carbonate of lime is required to neutralize the red color.

Again the question arises: how can a yellow-burning clay, which has been exposed to the air, in order that calcic ferric silicate, or calcic ferric oxide may be formed, exhibit a second time a red coloration on its surface? The analyses of the above mentioned bricks show that the yellow body of the brick from the brickyard at Neuhof contains $\frac{1}{2}$ per cent of sulphuric acid, while the red crust contains 9 per cent. In the other brick from Szegedin there is a still more striking difference between the brick itself and the crust. The brick contains about $\frac{3}{4}$ per cent of sulphuric acid, while this amount is increased to nearly 20 per cent in the crust.

This is very interesting. A chemist will understand without further explanation, that the red color must appear in the latter case, since sulphuric acid and lime form gypsum and the temperature necessary to burn the brick yellow, is not sufficient to decompose the gypsum. The lime is attacked by the sulphuric acid and, at this temperature, has no more effect upon further chemical action than if it were not present. It serves merely as a lean constituent.

The lime cannot form a chemical compound with the iron, since the sulphuric acid holds it in check, therefore the red color of the iron must appear again.

The presence of sulphuric acid in the crust cannot be accounted for in any other way than that it comes from the fuel.

These phenomena are common in all brickyards, and the causes cannot be accidental. Sulphur is present, as we know, in all kinds of fuel, especially in coal. Coal often contains a large amount of iron pyrites, which is the real source of this sulphuric acid, so there can be no doubt that a large quantity of sulphur gets into the bricks from the fuel.

How can the admixture of sulphuric acid and the consequent discoloration of these bricks be avoided? Sulphuric acid is not formed except when steam is present. This fact indicates that the water-smoking process must be carefully watched. It is advisable that the bricks be as dry as possible when they are put into the kiln, and that a kind of fuel be used which contains very little sulphur or none at all. If these precautions are taken, the phenomenon cannot appear.

At first sulphurous acid is formed, but this is of no consequence, unless this sulphurous acid is converted into sulphuric acid, which takes place only when water is present.

Practical brickworkers often shrug their shoulders at theoret-

ical scientists, because the latter do not understand the routine of practical manufacture, but here is a case where simple analyses have not only determined the cause of a troublesome feature in manufacture but also indicated the means by which discolorations may be obviated.

The Natural Colors and the Discoloration of Light Colored Bricks.

When bricks are to be used in the outer facing of buildings, it is important that their color should be uniform, at least that the different shades should be within certain limits, not too far apart. Even though a certain monotony is avoided when the single bricks are contrasted with each other by slightly differing shades of color, the material should, as a whole, present a uniform appearance. Sharp contrasts make a disagreeable impression upon the eye of the observer, especially in the same kind of material.

Such burning questions have arisen concerning the cause of the coloring in bricks, the conditions under which the discolorations and efflorescences appear, and the means by which a controlling influence may be exercised upon the color of bricks, that a constant impetus has been given to extensive, though often fruitless and expensive experiments with different kinds of kilns, fuel, etc.

Although the observations and investigations described in this paper are not exhaustive enough to furnish entirely satisfactory information on this subject, yet it is hoped that some light will be thrown upon a field which has up to this time received too little scientific study, and that further investigation and experiments will receive encouragement. My own researches in this direction are by no means concluded.

Since the light-colored brick materials present the greatest difficulties to the brickmaker in regard to the color of the body and surface of the bricks, these shall receive especial attention in our discussion.

In our examination of the causes of the coloring of bricks we shall start from the center of the brick. Four different phenomena must be sharply distinguished here, because they result from entirely different processes.

1. The color of the body of the brick, which can be determined from the fracture;
2. The color of the body of the brick at or near the outer surface, so far as this differs from the color of the inside or main body of the material.

3. The color of the surface, caused by some substance either foreign to the material of the brick, or derived from it during the drying, watersmoking, or firing, that is, efflorescence, incrustation, etc.

4. The color of the surface, caused by some substance foreign to the material, but formed upon the surface of the brick after the firing, either in the stack room or even after setting in the wall.

1. Clay in its purest state, which presents itself to our imagination as a compound of nothing but alumina, silicic acid, and water, and which most nearly approaches this ideal in porcelain-earth, or pipe-clay, contains few coloring constituents, or none at all, and therefore always appears as a pure white mass after firing. Such a material does not, for very apparent and valid reasons, come into consideration in the manufacture of bricks. Its cold whiteness would not satisfy the aesthetic taste.

But, since all the materials which have any practical value in the manufacture of bricks have been derived from a great variety of minerals, through weathering and mechanical breaking, they contain, besides the substances mentioned, others which, according to their kind and quantity, impart to the bricks a certain color, often very pronounced, or which at least exercise some influence upon the surface coloring. These are, above all, compounds of iron and manganese; further, lime, magnesia, alkalis, chlorine and sulphuric acid or sulphur compounds.

It is only the first two which can be looked upon as direct coloring constituents of all brick clays, since their compounds alone produce a marked color, yet the colors show the greatest diversity, according to the quantity in which the coloring agent is present, the simultaneous presence of other constituents, especially lime, magnesia and alkalis, and the physical condition of the material.

On the other hand, the above mentioned white-colored compounds of lime, magnesia and alkalis can be mentioned here among coloring agents only in so far as they modify the shade of the latter, while the compounds of chlorine and sulphur have no influence except upon the coloring of the surface, in incrustations and efflorescences.

The colors produced by the compounds of iron vary according to the state of oxidation in which these compounds occur. In the presence of ferrous compounds,* the color ranges through all shades of green to black; in the presence of ferric oxide,

from rose-color to blackish red, and when large quantities of lime are also present, through all shades of yellow.

Manganese occurs only when iron is present, and only in comparatively small quantities. The colors of its oxides range through all shades of brown to black.

It is well known, that ferric oxide, which we must look upon as the only coloring agent in the great majority of cases, produces a great variety of shades of color, varying from yellowish red to violet black, according to the manner of its distribution, a darker color always appearing when the clay was exposed to a high temperature. At a low temperature, iron oxide, if present in pure iron salts, sulphate of iron for example, has the color of red-lead, which becomes darker as the temperature is increased, and in the intense white heat, where its greatest condensation is reached, assumes a dark violet color.

Owing to this property of iron oxide it may be assumed at the outset, and this theory is confirmed by experience, that the color it imparts to brick clay will be darker in proportion as the temperature of the clay is increased, if the amount of iron oxide is not increased during the firing. Consequently the practical brick-maker finds in the appearance of an empirically determined color in the bricks the test of the thoroughness of the firing.

This power to produce a red color is retained by the iron oxide so long as the clay mass retains its porous character. It is only when the clay passes into the clinker state or is fused, that the color appears which large quantities of iron always impart to glassy fluxes, namely, black.

*In bricks which have not become dense by clinkering it is doubtful whether ferrous oxide occurs under ordinary conditions, i. e., when a dark color has not been produced intentionally by so-called "steaming," by which process the ferric oxide is reduced to ferrous oxide or iron metal, and up to this time this has not been proved. There is therefore no reason arising from the properties of the iron and the physical nature of the porous material, to assume any considerable retention or reformation of the ferrous oxide. Even when there is considerable coal in the clay, a condition favorable to the formation of ferrous oxide, as in the clay from Fürstenwald, the most pure and intense coloring of the ferric oxide appears. It is only in clinker and fused material that ferrous oxide may be expected under special conditions. Cf. the article by Prof. Dr. Remelé, "Notizblatt," 1867, p. 160, and 1868, p. 173.

The case is different when the colorless clay material contains calcium carbonate in addition to the iron oxide, as it often does. In the heat the lime acts as a flux and causes slagging much earlier than it would otherwise occur. A silicate is formed which absorbs the iron oxide and lime, along with the constituents of the clay, and this compound has a white or yellow color, when there is a certain proportion of lime and iron oxide.

This compound is not formed until slagging begins, and the coloring power of the iron oxide is not neutralized until this point is reached. At a lower temperature this power remains in force. Therefore clay containing lime and iron exhibits in a weak glow-fire the red color given by the iron oxide. This color vanishes as the heat is increased, and finally passes through flesh red and white into a more or less deep yellow, or yellowish green, and finally into green or black when complete vitrification is reached.

Of course there must be a certain relation between the quantity of iron oxide and lime in order that the red coloring property of the iron compounds may be neutralized, but the analyses of clay made up to this time have not given definite information on this point.

An example is furnished by the clay from Freienwald and Rüdersdorf,* specimens of which have been analyzed for our association in the Berg-Academy. In this clay the red coloring property of the iron oxide is not neutralized, but it is in the clay from Neuhoof near Stralsund, which will be described below.

There is a gap at this point in the series of investigations which have been made thus far and it remains for future research to fill it out. There must be, of course, some fixed law in regard to the proportion in which iron and lime, the chief factors in the coloring of bricks, stand toward each other when the power of the iron to produce its original, characteristic red color is neutralized. If, by means of an acid, the lime is removed from a clay which naturally burns yellow, that is, one in which both iron and lime are present, the usual property of the iron appears again, and the clay burns with a shade of red corresponding to the amount of iron.

Definite information is lacking also with regard to the influence of the manganese and magnesia, but this is of less importance, since these substances are found in clay only in comparatively small quantities, and when present, are always accompanied

* Cf., "Notizblatt," 1867, p. 119.

by much greater quantities of iron oxide or lime, so their effect upon the color does not easily become apparent.

With these seemingly simple factors the whole wide range of colors noticed in bricks has been stated. Yet in view of the variations to which the coloring influences are in reality subject, such as the quantity of the coloring substances, the physical condition of the material, the varying degree of heat, there is sufficient explanation, if not an exhaustive treatment, of the profusion of different shades, even if no account is taken of the discolorations by incrustation of ashes and efflorescence.

2. The above mentioned characteristic colorings of bricks apply only to the clay material in bulk, that is, to the body of the brick, since this is more or less removed from the external chemical and physical influences during the operations to which the brick is subjected in order to become an article of commerce. The shade of its color is therefore due almost entirely to the greater or less degree of heat.

It is different with the color in the vicinity of the surface. Here oxidizing and reducing influences act more readily. All substances derived from the furnace gases are concentrated here, and therefore all possible colors are displayed, while there is a certain constancy in the color of the body of the brick.

In order to explain the phenomena which come under this head, a distinction must be made between the colors exhibited by the clay material itself in the vicinity of the surface, and those which are due to the deposit of a different colored stratum upon the clay. The former are real discolorations, the latter incrustations. The latter, as well as efflorescences, etc., are often wrongly confounded with the former.

The discolorations caused by a chemical action of the furnace gases on the clay are less annoying in the case of red bricks, than of light colored ones, which are more sensitive in their color, especially yellow bricks. The reason is that the real clay material, as well as the coloring iron oxide, has less tendency to chemical action and is rather indifferent to the substances contained in the furnace gases. Here they can almost always be recognised, even from the external appearance, either as slagging, caused by the absorption of alkaline vapors, or vitrification, or a reduction of the iron oxide to black silicate of ferrous oxide.

The yellow bricks present a different case, as the lime contained in them has a strong affinity for some of the impurities which are always present in furnace gases. Accordingly we should expect to find the discolorations which are most annoying to the

brickmaker more frequently in light-colored bricks than in red ones, and ample confirmation of this is afforded in actual practice.

On a former occasion* I have referred to the influence which the constituents of the furnace gases have upon the clay under certain conditions, especially during the watersmoking process, in order to show that when generator gas is used in firing the kiln, the same discolorations will make their appearance which are dreaded in direct firing with solid fuel, and that those who imagine the use of gas will do away at one stroke with the difficulties of former operations, are pursuing a Utopian phantom.

The experiments described below confirm fully the theory which I formerly advanced.

The most frequently recurring discolorations of light-colored bricks are those which are indicated by red or reddish brown flames on the exposed surfaces, while the protected parts are yellow. Although these discolorations are liable to appear when any kind of fuel is used, they are most marked when coal is employed for firing, and it has become customary in many cases, especially in annular kilns, to avoid as much as possible the use of hard coal when good light-colored bricks are desired.

A distinction should be made here between the red colorations which are the result of imperfect firing, recognizable by the fact that they appear in the core of the brick or on the parts covered in the kiln, while the rest of the brick is light colored, and those which are formed on the exposed surfaces by the furnace gas, and which do not disappear even in the hottest fire. Sometimes both kinds of coloring are exhibited in the same brick, the core being red, the part near the surface yellow, and the outer surface itself red. These two kinds of red coloring are due to different causes: The inner red is due to the fact that the temperature was not raised high enough to neutralize the red coloring of the iron oxide by the formation of a silicate of lime. The outer red appears because the lime on the surface, being already combined, is rendered incapable of entering into the above mentioned silicate.

The red discolorations of yellow bricks appear in the fracture as a stratum, varying usually from the thickness of a sheet of paper to one millimeter, and most highly colored at the surface of the brick. Sometimes the stratum is thicker and the color very marked.

A particularly good specimen of this sort, with a colored stratum about 5 millimeters thick in some places, taken from the brickyard of Herr Hecht, in NeuhoF, near Stralsund, furnished

*Notizblatt, 1872, p. 165.

me the opportunity for an investigation which yielded a surprising result. The core of the brick was pure yellowish white, the outer surface dark blood red, gradually shading off toward the center. The brick had been burned in an annular kiln with English coal. Splinters were struck off from the outer colored crust, where it was highly colored, and these were pulverized and analysed.

At the same time the yellow core of the brick was examined by Herr Dr. Aron, exactly the same method being employed in both cases.

The analyses gave the following result:

| | Red part. | Yellow part. |
|-----------------------|------------------------|-------------------------|
| Silicic Acid | 63.71 per cent | 71.25 per cent. |
| Alumina | 9.81 per cent. | 8.60 per cent. |
| Iron Oxide | 5.16 per cent. | 5.92 per cent. |
| Lime | 8.72 per cent. | 9.24 per cent. |
| Magnesia | 2.20 per cent. | 1.89 per cent. |
| Sulphuric Acid* | 8.49 per cent. | .61 per cent. |
| Manganese..... | | traces. |
| Chlorine..... | traces. | |
| Alkalies | 1.90 per cent. | 2.49 per cent. |
| | <u>99.99 per cent.</u> | <u>100.00 per cent.</u> |

*It was not to be expected at the outset that the brick material would have exactly the same composition in all its parts, since the fracture of the brick showed that the mass was not perfectly homogeneous. But deducting the sulphuric acid in the red colored part from 8.49 per cent or 19.58 per cent, which can for the most part be abolished only during the firing, and estimating the percentage of the rest, the composition of the colored stratum is as follows:

| | In the brick from Neuhof. | In the brick from Szegedin. |
|----------------------------------|------------------------------|--------------------------------|
| Silicic acid, per cent..... | 69.62 | 56.86 |
| Alumina, per cent | 10.72 | 12.83 |
| Iron oxide, per cent..... | 5.88 | 5.58 |
| Lime, per cent..... | 9.53 | 15.82 |
| Magnesia, per cent..... | 2.41 | 4.39 |
| Manganese, per cent..... | | |
| Chlorine, per cent..... | | |
| Alkalies and loss, per cent..... | 2.14 | 2.78 |
| Water, per cent..... | | |
| | <u>100.30</u> | <u>98.24</u> |

There is no essential difference therefore between this and the yellow colored part.

The difference between the analyses in the proportion of sulphuric acid is very striking and characteristic. In both cases the sulphuric acid must be considered as combined with the lime and, since 40 parts by weight unite with 28 parts by weight of alumina to form gypsum, it would correspond to 1.04 per cent of gypsum in the yellow part of the bricks, and this proportion would be increased to 14.43 per cent in the red part.

Let us compare the amount of oxygen in the lime not combined with the sulphuric acid, and in the iron oxide.† The lime that is combined need not be considered at all in the formation of the silicate, since the gypsum is not decomposed at the temperature at which bricks are fired.—The proportion of iron oxide to lime is 1:1.34 in the red part, but 1:1.58 in the yellow part. Therefore with equal parts of iron oxide the yellow part contains five times as much lime for the formation of the silicate which gives the yellow color.

A similar examination of the clay analyses on page 119, "Notizblatt," 1872, shows the following proportions: In the pale red clay of Herr O. Oppenheim of Rüdersdorf, where there is a larger percentage of iron, the proportion is 1 to 1.11; in the dark red clay of Herr Kuhnheim, councillor of commerce, in the alum works near Freienwald, it is 1 to .35, that is, almost the same as that found in the red part of the brick from Neuhof.

An equally characteristic view of the phenomenon is furnished by the analysis of a brick from the society for brickwork and building of Szegedin. It is a light, porous mass, formed from a fine lean clay, of a sulphur yellow color inside, and a very dark violet red on the outside. The color stratum, which is about 10 mm. in thickness, is darkest on the outer surface and shades off through red into yellow toward the center. An analysis of the darkest parts on the outside and the yellow inside resulted as follows:

†It amounts to 1.78 per cent in the red part, 8.61 per cent in the yellow part.

| | Reddish Violet Part. | Yellow Part. |
|------------------------|------------------------|------------------------|
| Silicic acid | 45.73 per cent. | 56.07 per cent. |
| Alumina | 10.22 per cent. | 14.02 per cent. |
| Iron oxide | 4.49 per cent. | 5.49 per cent. |
| Lime | 12.81 per cent. | 16.53 per cent. |
| Magnesia | 3.53 per cent. | 4.50 per cent. |
| Sulphuric acid*..... | 19.58 per cent. | .74 per cent. |
| Alkalis and loss | 2.24 per cent. | 2.66 per cent. |
| Water | 1.40 per cent. | .39 per cent. |
| | <hr/> 100.00 per cent. | <hr/> 100.40 per cent. |

The enormously high percentage of sulphuric acid in the discolored part shows that the same causes are at work here as in case discussed above, only that here the process of the combining of the lime is further advanced. For the 19.58 per cent of sulphuric acid there is necessary for the formation of gypsum 13.70 per cent of lime. Consequently it must be assumed that all the lime is combined with the sulphuric acid, and in addition, a part of the magnesia, .64 per cent, must be converted into a salt sulphate.

In the yellow part of the brick the proportion of iron oxide and lime, as determined by a comparison similar to the one above, is 1 to 2.86 in the yellow core of the brick, that is, even more favorable for the neutralizing of the red coloring of the iron oxide, than in the brick from Neuhof. In the discolored stratum the proportion has sunk from 1 to 0; that is, the lime has here lost its power to influence the ordinary red coloring property of the iron, because, having entered into the silicate of a lime-iron compound, it is completely combined with the sulphuric acid.

If we ask now, to what this surprisingly great proportion of sulphuric acid in the outer portions of the discolored brick is due, there is but one answer: to the furnace gas, for this is the only influence to which the brick is exposed during the reddening process.

All kinds of fuel, except wood, contain sulphur; peat having the smallest amount, brown coal a larger amount, and mineral coal the largest.† During the firing the sulphur is volatilized in the form of sulphurous acid.

*Refer to footnote on page 238.

†The amount of pyrites in the mineral coal varies from 1 to 5 per cent, and may be called 2 per cent on an average.

Under favorable conditions, this sulphurous acid may be oxidized to sulphuric acid, thus withdrawing the lime for the formation of a strongly calcareous, yellow colored silicate of ferrous oxide, so that the original coloring power of the iron oxide is preserved intact. This happens particularly, perhaps exclusively, during the water-smoking process, if an opportunity is given here for the water vapors to condense on the surfaces of the brick, and if the lime of the clay mass is also in action at the same time, as well as the excess oxygen of the furnace gases.

3. The above described discolorations should not be confounded with those which are deposited upon the surfaces of the brick during the firing as white or gray coatings, which are, however, not real colorings of the clay mass, and do not penetrate to its center. It seems that the chemical properties of the clay have less effect in their formation than the physical properties.

These coatings consist either of salty efflorescences, which originated in the drying or watersmoking process, and became fixed in firing by decomposition, or by flue dust which adhered to the surfaces of the brick.

The difference between these two kinds of coating, of different origin, can easily be determined by means of a microscope.

The former are peculiar to fat clays especially, and can frequently be detected, on close observation, on the surface of air dried bricks, particularly on the edges. They are more likely to occur, the smoother and denser the surface, and therefore are most common on pressed bricks and the smooth surfaces of machine-made bricks, rarely appearing on the rough surfaces of the ordinary backing bricks molded in sand. With the aid of a glass they can be distinguished as wartlike joints on the surface, usually white. Their origin is due to the circumstance that the water which permeates the clay, especially if sulphuric acid or chlorine is present, contains soluble salts which are deposited in solid form, when it evaporates.

Now if the clay is lean and porous, this evaporation takes place not only on the surface, but also in the brick mass, the precipitated salts being thus distributed over a large space.

If, however, the surface of the brick is very dense, or if the pores on the surface are filled with water, owing to faulty water-smoking, so that the air cannot penetrate by diffusion into the interior of the brick, the evaporation and consequent precipitation of salts from the water can take place only at the surface, addi-

tional water being constantly drawn from the interior by capillary action.

In this case, therefore, it is especially the impurities of the clay which have a detrimental effect upon the color of the surface by giving occasion for the formation of soluble salts. These impurities are sulphuric acid (or pyrites), chlorine, magnesia and alkalis.

Since these efflorescences do not in many cases appear until the watersmoking process, and then only when water vapors are condensed upon the bricks, they can often be avoided by managing the watersmoking with especial care.

But efflorescence and incrustations are not due solely to the soluble salts contained in the clay. They often come from outside during the firing and are absorbed by the moist surfaces of the watersmoking bricks.

Sulphuric acid has already been mentioned as one of the causes, but it is often the alkalis, which, after being volatilized from the constituent ashes in the fire, are again precipitated in the colder parts. Light incrustations often appear on the covers and pipes of annular kilns; an incrustation of this sort appeared in the annular lime kiln of Herr Fr. Hoffmann, an architect on the Nordhafen in Berlin, which proved to be a mixture of potassium and sodium sulphate and potassium and sodium chlorate.

From these incrustations, which are the ones occurring most frequently, those produced by flue dust are easily distinguished. The former usually appear under the microscope as white wartlike joints, the latter are darker, usually of a gray or brown color, and are composed of little splintery kernels, which generally adhere to the moist surface of the brick upon which they have been precipitated during the watersmoking process, but are sometimes only loosely combined with the clay, so that they can even be wiped off from clinkerlike sintered bricks, without leaving any noticeable residuum.

4. The fourth class of colorations comprises those which are developed only after the bricks are already manufactured or even after they have been used in building, and their appearance is usually an indication that the bricks are of a perishable character. These are, for the most part, salty efflorescences, which pursue their work of destruction quietly, by means of the repeated disappearance and reappearance of the crystalline forms, or organic formations which reach the same goal in a longer time and with less energy. Moisture is the element of both.

The destruction of bricks by means of saline formations, which

advance outwards from the center to the surface, is particularly noticeable in slightly burned porous material, in the manufacture of which the heat was not sufficient to destroy the soluble salts present in the clay, or to convert their elements into the insoluble compounds of silicic acid.

These saline efflorescences, commonly called saltpeter, consist frequently of a double carbonate of sodium, of sulphates, especially those of sodium and magnesium, of compounds of chlorine and other substances, but they do not contain saltpeter except when the bricks come in contact with decaying organic matter.

There is probably no reason to attribute the appearance of so-called saltpeter to the influence of lower organisms, as is often done.

In the case of light-colored bricks, and only these, not the red or dark colored ones, we may however see the action of organisms, and it is indicated here in an especially annoying manner, by a deep green or yellow coloring of the brick surfaces.

These are microscopic growths, algae, which grow rampant upon the most porous surface, draw their sustenance from it, and, as one generation after another dies off, cover it with a black mouldy substance. It seems to be less the nature of the material than its color, which favors the growth of these organisms, for they appear not only on the ordinary yellow bricks from calcareous material, but also quite regularly on refractory clay bricks and fire-bricks, if they are exposed to moisture and shielded from direct sunlight. They appear only on the light parts of the brick, never on the spots where there are dark incrustations.

It is difficult to guard against an enemy like this, which often does not appear until the bricks, which were of perfect color at the time they were used in construction, are no longer easily accessible, after the discoloration has appeared, for the destruction of the vegetable growth.

The only means of destroying this foe to the color of light bricks seems to be killing by means of caustics. Herr Dr. Frühling has recommended painting brickwork covered with a green incrustation with a solution of calcium sulphide, but it is not certain that this will give protection for any length of time, since it is itself subject to rapid change. Perhaps something which acts as a permanent poison for organic growth should be used, such as zinc sulphate (but not zinc chloride, for fear of saline efflorescence), or arsenic.

The Coloring of Bricks.

An examination of the clays used for porcelain or earthenware, which burn pure white, or nearly so, shows that they always contain, as essential constituents, alumina, silicic acid, and water, but only very small quantities of other substances. These clays have been formed by the action of the weather upon feldspar, and usually remain in the place where they originated. But if they are transported by means of streams, they must inevitably become mixed with other substances, which originated in the same manner in other localities, by the action of the weather, or by trituration, and which, therefore, impart a more or less pronounced color to the products made from them. Such materials are those used in the manufacture of bricks.

In actual practice, the number of ingredients which affect the coloring of the clay is very limited. Aside from the substances which occur infrequently and in very small quantities, seldom more than one per cent, and which have no appreciable effect upon the color, such as titanitic acid, vanadic acid, etc., we need to consider only iron and manganic oxide, and, further, the carbonates of lime and magnesia, which produce so many different colors in bricks. There is great variation in the colors, according to the amount and distribution of the coloring ingredient, the temperature to which the bricks are exposed, the structure of the material, especially as regards porosity, and finally, according to the difference in the action of the furnace gases. Two clays of exactly the same composition will not necessarily exhibit the same colors in burning, but may differ widely, owing to differences in the distribution of the iron oxide, and the structure of the brick. Therefore it may happen, that the coloring of the iron oxide may be less marked in a material containing much iron oxide, than in one which contains less.

Let me say, first, that the colors in the unburned clay have no connection whatever with the colors which appear after firing, and it is erroneous to assume that the finished product will have the same color as clay. The iron, which has been washed into the clay in the form of iron silicates, ferric hydrate, or ferric oxide, or ferrous compounds, may show great variation in color, ranging from red and yellow to gray or bluish green. Besides this, it is frequently accompanied by organic matter.

Aside from the iron oxide, manganic oxide is the only metal which produces any color in the firing, but usually we need not take this into account, since it always occurs in connection with

the ferric oxide and, ordinarily, in small quantities compared with the latter.

In many clays carbonates of lime and magnesia are found in considerable quantities, which, although pure white themselves, nevertheless modify, by their presence, the action of the ferric oxide.

The colors exhibited in clay products are therefore conditioned by a number of factors acting conjointly, some having a greater influence, others less.

The chief influences are the following:

1. The amount of ferric oxide in the clay.
2. The other ingredients of the clay.
3. The composition of the furnace gases during the firing.
4. The degree of slagging.
5. The temperature reached in the firing.

Let us examine these five factors separately. 1. Ferric oxide is, in its native state, a red substance. When exposed to a low temperature, its color is yellowish red, if it is finely distributed throughout the clay. When the temperature is increased, it becomes denser and darker, and in an intense heat, it has a dark reddish blue color. But even this red color varies somewhat, according to the manner in which the oxide has been formed from different substances, shading sometimes into brown or blue. This color does not last, however, unless the ferric oxide is heated in an atmosphere containing an excess of oxygen. But if the heating takes place in the presence of reducing gases, carbonic oxide or carburetted hydrogen, it is reduced to ferrous oxide, or to intermediate stages of ferrous and ferric oxide, or of ferrous oxide and metallic iron, finally, to metallic iron, and in all these compounds it assumes a blackish color.

When on the other hand, these substances are heated in air containing oxygen, they take up again the lost oxygen, again give opportunity for the formation of ferric oxide, and the red color is again restored, although it is usually a different shade from the original ferric oxide.

In general, all the phenomena of color in clay products take this course. The intensity of color depends, ordinarily, upon the amount of ferric oxide present, the color being deeper, the greater the amount of iron.

2. A decided influence is also exerted upon the color by the substances which usually show only a white color in burning, such as alumina, lime and magnesia. Clay containing a small amount

of iron oxide, and a large amount of alumina, will, when fired at a high temperature, assume only a more or less yellow, or yellowish brown color, which passes gradually through all shades of yellowish brown to reddish brown, as the alumina decreases and the iron oxide increases in amount. It is only when there is more than five per cent of iron oxide present, that a decided red color appears, which deepens as the iron oxide increases.

Just as the color grows paler when a large amount of alumina is present, so it does also in the presence of carbonate of lime, which is often accompanied by a still smaller quantity of carbonate of magnesia. In the latter case, as in the former, the color of the ferric oxide grows paler, as the temperature of the wares is raised.

If the amount of lime is twice as great as that of the ferric oxide, the red color of the latter disappears altogether, when the temperature is sufficiently high, and gives place to a yellowish green color.

In general, therefore, nothing more can be said than this; a red color will be exhibited only by those clays which contain a large quantity of iron and a moderate or small quantity of alumina and lime. If the alumina decreases in amount simultaneously with the ferric oxide, the color will be more or less yellowish brown, or yellow, but if the clay contains carbonates, it will pass into a yellowish green.

If therefore other shades of color are desired, than those which can be secured from the clay itself, if the color is to be changed from red to yellow in the firing, this can be accomplished by adding a clay which burns white, or with little color, and contains as much alumina as possible.

The colors will then range through red, brown, yellowish brown and yellow. The same result may be obtained by adding some calcareous material, such as chalk, or lime-marl.

In order to change the color in firing from yellow to red, a highly ferruginous material must be added, such as ferruginous clay, ochre, or swamp-ore. This addition will produce the desired result directly, if the clay does not contain lime, but if lime is present, the effect will be less noticeable, in proportion as the lime is abundant. Of course the heat necessary for firing will have to be changed also, on account of these admixtures. As a rule, the firing heat must be increased by the addition of light burning, argillaceous earth, and decreased by carbonate of lime, or ferric oxide.

3. The composition of the furnace gases used in firing is an

item of very great importance for the coloring of the clay products. It is well known that the construction of the kiln has an influence in this regard, and those who have used different kinds of kilns know that with the same material the colors vary according as the clay is burned in one kiln or another.

The cause of these differences will become apparent if we consider the action of the ferric oxide in an oxidizing and reducing fire. The sulphur in the coal has some influence also.

As I have already explained, the compounds of ferric oxide are always transformed into ferrous compounds by reducing gases, such as carbonic oxide, carburetted hydrogen and hydrogen, or into metallic iron, if ferric oxide is present in the clay in a free state. This causes a gray color in the clay. If a sample is taken from the kiln during the firing, this gray color will be seen to have deepened to black, when iron is present in large quantities.

In an oxidizing atmosphere, if the sample is still porous, the ferrous oxide or metallic iron passes rapidly again into the red or yellow-coloring ferric oxide. The more compact the structure is, and the less the surface thus exposed for the access of oxygen, so much slower is the re-formation of ferric oxide, and if the brick is quite compact, it remains black or gray, the surface, at most, assuming a brownish or reddish color.

In general, we have in our kilns an alternating oxidizing and reducing action, the change taking place at greater or less intervals in the different kinds of kilns. In non-continuous kilns the reduction occurs especially in the first stage of the firing, becoming more infrequent and weaker in the last stage, while in continuous kilns the reducing action remains uniform. In all kilns the wares are cooled in an oxidizing atmosphere, unless pains is taken to secure a reducing action during the cooling stage by means of "steaming." The result secured thereby is, that the reducing action is still noticeable to a greater or less degree, after the cooling, manifesting itself by a color which sometimes approaches green, sometimes gray—the former especially in calcareous materials, the latter in the non-calcareous materials, which burn yellow and red.

The sulphur of the coal, which appears in the furnace gases in the form of sulphuric acid, also plays an important part in the phenomena of color. This is especially conspicuous in the case of calcareous clays, since a sulphate of lime is formed on the surface.

If the lime cannot, for this reason, enter into the silicate which

is formed, the ferric oxide is free to affect the color, unhindered by the lime, and then a red color, often very deep, appears on the surfaces exposed to the fire. To be sure, the red spots disappear again, on account of the reducing action, but since the conditions of slagging have been altered, by reason of the deposit of sulphuric acid, the colorings on the surfaces which have once been spotted are, as a rule, still distinguishable by a different shade of color.

4. The extent to which the clay becomes slagged during the firing has, likewise, some influence upon its color. When the material is porous, containing many air cells, the colors become constantly lighter, but when the structure is more compact, they become deeper, the proportion of iron being the same in both cases.

5. The different temperatures at which firing takes place also cause differences in color. We have already seen that the ferric oxide, which produces color, becomes darker as the temperature is raised. The same thing is characteristic of its compounds, and we see, therefore, that the clays burned at a high temperature have, in general, a darker color. But the reverse is true when the clay contains a small amount of carbonate of lime, not enough, however, to neutralize entirely the red coloring caused by the ferric oxide. In this case the lime has a disturbing effect upon the color, even at a higher temperature, and therefore the color becomes lighter when the firing is more severe. In all non-calcareous substances the properties of the ferric oxide alone are active.

The facts presented serve to explain only those phenomena of color exhibited in materials on the surface of which there is not a thin coating, and the fracture of which does not show a diminution in the intensity of color, that is, materials which are free from incrustations.

As a rule the incrustations are caused by salts, usually sulphates, which become white in firing, or slightly colored, if they have been partially slagged with the clay. The salts occur either in a free state in the clay, or are found in the water used to soften it. During the drying process they reach the free surfaces where evaporation takes place and are here deposited as a fine crystalline coating, or else they owe their origin to the action of the fire in the first stages of the firing. In the latter case they are caused by the condensation of the water in the furnace gases upon the surfaces of the bricks. The furnace gases contain, in addition to the water, certain substances from the flue-dust,

which become volatilized at a higher temperature, and also sulphuric acid, a product of the combustion of iron pyrites, always present in the coal, and finally particles from the flying ashes.

If water is condensed upon the surfaces of the bricks it is evident that these substances will be deposited upon the wares, and they are usually not without considerable influence upon the phenomena of color.

We can tell by inspection whether these deposits were formed before the firing, or whether they are due to the influence of the furnace gases in the first stage of the firing. In the former case the surfaces upon which the wares lay during the drying process are free from deposits, and in the latter case those which were protected when the wares were put into the kiln. As these surfaces are not always identical, we can easily determine the time when the deposits must have originated. In the firing these saline efflorescences are generally so thoroughly slagged upon the surfaces, that they cannot be removed, and by reason of this slagging their composition has been altered, and they have become insoluble to such an extent that the wares usually retain permanently traces of this coloring upon their surfaces.

But it is possible that bricks may change their color, even after they have been used in building. Salts which have remained without decomposition in the pores of the bricks, may come to the surface when they are moistened with water, and here take the form of efflorescences. These are frequently sulphates which were originally in the clay, or were formed in firing by the action of sulphuric acid from the coal, and were not removed by the reducing fire. The efflorescences are white in the latter case, and may be obviated by securing a reducing action of the furnace gas in the last stage of the firing. But they may be green or yellowish green compounds of vanadic acid, which is always present in clay, though in very small quantities. These can also be avoided by a reducing action of the furnace gas, since the vanadic acid is reduced and is retained in the clay as vanadic oxide. The colors produced by a larger or smaller amount of ferric oxide in the clay can be determined by means of a number of mixtures of different clays, which contain a known quantity of ferric oxide. In the factory of Herr March, councillor of commerce, specimens secured for this purpose were mixed in definite proportions, two clays always being mixed in such proportion that to 0.1, 0.2, 0.3, etc., of the first, there was added one part by weight of the second and then so on downwards with the second clay. Five kinds of clay were employed

for the mixtures. The clay containing the most iron, that from Helmstedt, contains 21.3 per cent of ferric oxide at a glow heat; the clay from Rathenow contains 8.02 per cent; that from Belgern, burning yellow, contains 4.63 per cent; that from Tschirn, 1.02 per cent; and that from Löthain, 8 per cent.

A comparison of the colors assumed by the clays with the amount of ferric oxide contained in them shows that the increase of the ferric oxide beyond a certain proportion has no appreciable effect upon the color, while a diminution of it produces noticeable variations in color. The specimens whose amount of ferric oxide lies between 21.3 and 8.5 per cent, do not differ appreciably in color. It is only when the amount of ferric oxide is reduced that marked variations in color appear. The mixtures become lighter and finally pass into white. A typical specimen is the clay from Belgern, which contains as much as 4.6 per cent of ferric oxide, and exhibits a deep yellow color. On the other hand a mixture of the clays of Löthain and Helmstedt, containing 4.2 per cent of ferric oxide, is pale red.

The results of the mixtures have been tabulated as follows:

TABLE I.

Helmstedt clay, containing 21.3 per cent of ferric oxide, mixed with Löthain clay, containing 0.8 per cent of ferric oxide.

| Helmstedt Clay. | Löthain Clay. | Color. | Ferric oxide, Per cent. |
|-----------------|---------------|----------------|----------------------------|
| Pure | | dark red | 21.3 |
| 10 parts. | 4 parts. | " | 15.4 |
| 10 " | 8 " | " | 12.2 |
| 10 " | 10 " | " | 11.0 |
| 8 " | 10 " | " | 9.9 |
| 6 " | 10 " | red | 8.5 |
| 5 " | 10 " | lighter red | 7.6 |
| 4 " | 10 " | still lighter | 6.6 |
| 3 " | 10 " | light red | 5.5 |
| 2 " | 10 " | yellow | 4.2 |
| 1 " | 10 " | light yellow | 2.7 |
| ½ " | 10 " | whitish yellow | 1.8 |
| ¼ " | 10 " | almost white | 1.3 |
| | Pure. | white | .8 |

TABLE II.

Rathenow clay (washed) containing 0.8 per cent of ferric oxide,
with Belgern clay, containing 4.6 per cent of ferric oxide.

| Rathenow Clay. | | Color. | Ferric oxide, Per cent. |
|----------------|---------|-----------|----------------------------|
| Pure. | | dark red | 8.0 |
| 10 parts. | 1 part. | | 7.7 |
| 10 " | 2 " | | 7.4 |
| 10 " | 4 " | | 7.0 |
| 10 " | 6 " | color | 6.7 |
| 10 " | 8 " | decreases | 6.5 |
| 10 " | 10 " | uniformly | 6.3 |
| 8 " | 10 " | in | 6.1 |
| 6 " | 10 " | intensity | 5.9 |
| 4 " | 10 " | | 5.6 |
| 2 " | 10 " | | 5.2 |
| 1 " | 10 " | | 4.9 |
| ½ " | 10 " | | 4.8 |
| | Pure. | yellow | 4.6 |

When the firing is more intense, the colors are somewhat darker, shading into brown, but diminishing uniformly in intensity.

TABLE III.

Helmstedt clay, containing 21.3 per cent of ferric oxide, and
the clay of Tschirn containing 1 per cent of ferric oxide.

| Helmstedt Clay. | Tschirn Clay. | Color. | Ferric oxide, Per cent. |
|-----------------|---------------|----------------|----------------------------|
| 10 parts. | 4 parts. | dark red | 15.5 |
| 10 " | 8 " | " | 12.3 |
| 8 " | 10 " | " | 10.0 |
| 6 " | 10 " | " | 8.6 |
| ½ " | 10 " | light yellow | 2.0 |
| ¼ " | 10 " | lighter yellow | 1.5 |
| | Pure. | almost white | 1.0 |

The specimens omitted between lines 4 and 5 give very varying results in color and are therefore not included in the table.

TABLE IV.

Belgern clay containing 4.6 per cent of ferric oxide, with
Löthain clay containing 0.8 per cent of ferric oxide.

| Belgern Clay. | Löthain Clay. | Color. | Ferric oxide, Per cent. |
|---------------|---------------|--------------|----------------------------|
| Pure. | | yellow | 4.6 |
| 10 parts. | 2 parts. | light yellow | 4.0 |
| 10 " | 6 " | " " | 3.2 |
| 10 " | 8 " | | 2.9 |
| 10 " | 10 " | | 2.7 |
| 8 " | 10 " | gradually | 2.5 |
| 6 " | 10 " | shading | 2.2 |
| 4 " | 10 " | into | 1.9 |
| 2 " | 10 " | white | 1.4 |
| 1 " | 10 " | | 1.1 |
| Pure. | | white | 0.8 |

In all these phenomena of color the effect of the ferric oxide is undoubtedly conditioned by its quantity, but that is not the only thing which we have to take into consideration. The chemical composition of the clay, the mechanical distribution of the ferric oxide, the coloring agent, also the intensity of the firing heat, and, finally, the action of the furnace gases upon the wares during the firing, are all conditions which affect the production of the shades of color.

Temperature and Composition of Furnace Gases in the Annular Kiln.

In a recent number of Dingler's Polytechnic Journal* there is an article by Ferdinand Fischer, of Hannover, on the burning of bricks in the annular kiln, in which the author gives the results of observations of temperature and analyses of furnace gases obtained in two annular kilns, each with fourteen chambers, near Hannover, one at Stöcken, the other on the Linden Hill.

The temperature was observed in every part of the kilns. The lower readings, up to 300° C., were taken with a suitably arranged mercury thermometer, the higher ones with an electric pyrometer from Siemens Bros., London, which has often been described in ceramic journals.

According to the readings taken, the highest temperature re-

*"The Burning of Bricks in the Annular Kiln." Dr. F. Fischer. Dingler's Polytechnisches Journal. 1878. pp. 228-432.

corded in the kiln at Stöcken was 1057° C., and the gases in the chimney escaped at a temperature of 108 or 172° C. In the kiln at Linden the highest temperature was 968° C., almost 100° lower, and the temperature of the escaping furnace gases was only 80° C.

The results of the observations, which are graphically represented by the author in two diagrams, are presented here in tabular form, the temperature at the beginning and end of each chamber being shown.

| ANNULAR KILN AT STÖCKEN. | | ANNULAR KILN AT LINDEN BERG. | |
|-------------------------------|----------------|-------------------------------|---------------|
| No. of Chamber. | Temperature. | No. of Chamber. | Temperature. |
| Preliminary heating | 8 80- 130°C. | Preliminary heating | 10 60- 80°C. |
| | 7 130- 210°C. | | 9 80-200°C. |
| | 6 210- 400°C. | | 8 200-440°C. |
| | 5 400- 700°C. | | 7½ 440-660°C. |
| Firing | 4 700- 880°C. | Firing | 7½ 660-800°C. |
| | 3 880-1057°C. | | 6 800-960°C. |
| Cooling | | | 5 960°C. |
| | | | 4½ 960-800°C. |
| | 2 1000- 600°C. | Cooling | 4½ 800-660°C. |
| | 1 600- 360°C. | | 3 660-490°C. |
| Used for emptying and filling | 14 360- 160°C. | | 2 490-300°C. |
| | 13 160- 80°C. | | 1 300-120°C. |
| | | | 14 120- 40°C. |
| Used for emptying and filling | 12 | Used for emptying and filling | 13 |
| | 11 | | 12 |
| | 10 | | 11 |
| | 9 | | |

It is especially interesting to note that in the Stöcken kiln, in which the burning is completed in 7 or 8 days, the temperature rises steadily to its highest point, and then falls immediately, just as steadily, while in the Linden kiln, which burns in 14 days, with more gradual increase and decrease, the highest temperature is maintained uniformly in a large part of the kiln, and consequently a greater uniformity in firing is assured.

From the figures given, it seems that the clays burned in these kilns were among the more easily fusible ones. Peclet's statement, that the temperature of brick kilns may be assumed as 600-700° C., gives probably too low an estimate. It seems rather to approximate the fusing point of silver, 960° C.

In addition to the observations of temperature, the analyses of the furnace gases in the above-mentioned kilns were given. The gases were analyzed at a point 3-10 of a meter below the arched

roof of the kiln, and also on the floor of the kiln. In general the specimens were selected alternately from top and bottom, and those which followed each other in direct succession placed together in the table. Those marked with an asterisk were taken out directly after the coal was put in.

On examining tables I and II, it becomes apparent that there is much more air in circulation, without affecting the generation

I. ANNULAR KILN AT STOCKEN, JULY 24, 1877.

| Beneath the Arched Roof. | | | | | On the Floor of the Kiln. | | | | |
|--------------------------|-------------------|--------------------|---------|-----------|---------------------------|-------------------|--------------------|---------|-----------|
| Time of Observation. | Carbonic Acid. | Carbonic Oxide. | Oxygen. | Nitrogen. | Time of Observation. | Carbonic Acid. | Carbonic Oxide. | Oxygen. | Nitrogen. |
| hr. min | | | | | hr. min | | | | |
| 9.45 | 4.1 | 0 | 16.6 | 79.3 | 10. | 7.5 | 0 | 12.9 | 79.6 |
| 10.10 | 4.4 | 0 | 16.4 | 79.2 | 11. | 9.1 | 0 | 11.4 | 79.5 |
| 11.05 | 5.1 | 0 | 15.6 | 79.3 | 11.10 | 11.7* | 0 | 8.7 | 79.6 |
| 11.18 | 6. | 0 | 14.6 | 79.4 | 11.28 | 11.1* | 0 | 9.3 | 79.6 |
| 11.37 | 5.2 | 0 | 15.6 | 79.2 | 11.45 | 9.6 | 0 | 10.9 | 79.5 |
| 12. | 5.8 | 0 | 14.8 | 79.4 | | | | | |
| 1.50 | 1.1 | 0 | 19.9 | 79. | 1.57 | 1.3 | 0 | 19.6 | 79.1 |
| 2.15 | 3. | 0 | 17.9 | 79.1 | 2.30 | 7.8 | 0 | 12.9 | 79.3 |
| 2.36 | 3.4 | 0 | 17.6 | 79. | 2.42 | 7.7 | 0 | 12.6 | 79.7 |
| 2.48 | 3.4 | 0 | 17.3 | 79.3 | 3.03 | 7.5 | 0 | 13. | 79.5 |
| | | | | | 3.12 | 8.3 | 0 | 12.3 | 79.4 |
| 3.17 | 3. | 0 | 17.9 | 79.1 | 3.22 | 7.8 | 0 | 12.8 | 79.4 |
| 3.28 | 3.2 | 0 | 17.6 | 79.2 | 3.33 | 10.0* | 0 | 10.2 | 79.8 |
| 3.39 | 3.8 | 0 | 17. | 79.2 | | | | | |
| 3.50 | 4.8 | 0 | 15.9 | 79.3 | 3.57 | 11.8 | 0 | 8.4 | 79.8 |
| 4.03 | 5.4 | 0 | 15.2 | 79.4 | 4.12 | 11.8 | 0 | 8.2 | 80.0 |
| 4.17 | 5.8 | 0 | 14.9 | 79.3 | 4.23 | 11.2 | 0 | 9.2 | 79.6 |
| 4.28 | 6.2 | 0 | 14.5 | 79.3 | 4.45 | 12.2 | 0 | 8. | 79.8 |
| 4.37 | 3.2 | 0 | 17.7 | 79.1 | 4.50 | 9.8 | 0 | 10.6 | 79.6 |
| 4.52 | 6. | 0 | 14.8 | 79.2 | 5.15 | 14.2* | 5 | 5.8 | 79.5 |
| 5.05 | 4.8 | 0 | 16.1 | 79.1 | 5.31 | 10.2 | 0 | 10.1 | 79.7 |
| 5.24 | 5. | 0 | 15.8 | 79.2 | 5.40 | 11.2 | 0 | 9.1 | 79.7 |

of heat, in the upper part of the kiln, than on the floor, and that more heat must consequently be generated in the latter place. Let us look at the figures in the middle of the tables. Of the 21 parts (by volume) of oxygen, which enter the kiln with 100 parts of fresh air, only 4.3 parts are really reduced to carbonic acid in the combustion of the coal, in the upper part of the kiln, beneath the vaulted roof. This is true of both kilns. On the floor, 8.4 parts are consumed in the Stöcken kiln and 8.2 at Linden; i. e., in

round numbers only 1-5 is consumed beneath the roof, and 2-5 on the floor. Such a combustion would be called extremely wasteful in a non-continuous kiln, and it occurs probably in hundreds of annular kilns, as they are now operated. Perhaps it is the rule, rather than the exception. But if, in spite of this fact, the annular kilns far surpass most other kilns in economy of

II. ANNULAR KILN AT LINDEN. SEPT. 24, 1877.

| Beneath the Arched Roof | | | | | On the Floor of the Kiln | | | | |
|-------------------------|---------------|----------------|---------|-----------|--------------------------|----------------|-----------------|---------|-----------|
| Time of Observation | Carbonic Acid | Carbonic Oxide | Oxygen. | Nitrogen. | Time of Observation. | Carbonic Acid. | Carbonic Oxide. | Oxygen. | Nitrogen. |
| hrs. min. | | | | | hrs. min. | | | | |
| 10.02 | 2.3 | 0 | 18.7 | 79 | 10.10 | 7.3 | 0 | 13.8 | 78.9 |
| 10.20 | 2.1 | 0 | 18.9 | 79 | 10.25 | 4.8 | 0 | 16.1 | 79.1 |
| | | | | | 10.35 | 5.4 | 0 | 15.4 | 79.2 |
| 10.44 | 2.4 | 0 | 18.6 | 79 | | | | | |
| 10.55 | 2.6 | 0 | 18.3 | 79.1 | 11.01 | 7 * | 0 | 13.8 | 79.2 |
| | | | | | 11.35 | 10.7 | 0 | 10 | 79.3 |
| 11.42 | 5.6 | 0 | 15.3 | 79.1 | 11.48 | 7.6 | 0 | 13.5 | 79.9 |
| 11.54 | 4.5 | 0 | 16.4 | 79.1 | 12 | 7.6 | 0 | 13.2 | 79.2 |
| 12.06 | 5.5 | 0 | 15.5 | 79 | 12.12 | 7 | 0 | 13.9 | 79.1 |
| 12.17 | 7.9* | 0 | 13.2 | 78.9 | 12.24 | 8.2 | 0 | 12.7 | 79.1 |
| 12.30 | 4.7 | 0 | 16.2 | 79 | | | | | |
| 12.39 | 4.3 | 0 | 16.7 | 79 | 12.45 | 18.4* | 0 | 2.2 | 79.4 |
| 12.51 | 5. | 0 | 16. | 79 | 12.59 | 6.2 | 0 | 14.6 | 79.2 |
| | | | | | 1.05 | 9.4* | 0 | 11.5 | 79.1 |
| 1.13 | 4.2 | 0 | 16.9 | 78.9 | 1.19 | 6.8 | 0 | 14.4 | 78.8 |
| | | | | | 1.26 | 8.5 | 0 | 12.4 | 79.1 |
| 1.32 | 4.8 | 0 | 16.3 | 78.9 | 1.40 | 6.7 | 0 | 14.3 | 79 |
| | | | | | 1.46 | 6.2* | 0 | 14.7 | 79.1 |
| | | | | | 1.52 | 10.6 | 0 | 10.2 | 79.2 |
| | | | | | 2 | 8.4 | 0 | 12.5 | 79.1 |
| 2.14 | 7.7 | 0 | 13.3 | 79 | 2.20 | 10.1* | 3.8 | 8.1 | 78 |
| 2.46 | 3.2 | 0 | 17.8 | 79 | | | | | |
| 2.56 | 3.1' | 0 | 17.7 | 79 | | | | | |

combustion, it is because the heat, when it has once been generated, is constantly utilized again, the escaping heat for the preliminary warming, the heat of the cooling bricks for bringing the furnace gas nearly to the temperature of the full fire. Thus the losses caused by excess of air are fully offset.

But the tables show also that, as a rule, there cannot be, with so great an excess of air, any production of gases which are still

combustible, and yet escape on account of lack of oxygen. It is true that carbonic oxide appeared only in a few cases, in small quantities, and immediately after the fire was stirred; furthermore, there was always more oxygen with it than was necessary for combustion, so that its appearance can be explained only by the unfinished process of firing.

But it is well known that the occasional appearance of unconsumed gases when oxygen is not present, is a necessary condition for the production of many colors, especially the light ones. On the other hand, the comparatively rare appearance of reducing gases, i. e., the still unconsumed decomposition products of the coal, affords an explanation for the difficulties which have hitherto been encountered in the manufacture of evenly colored face bricks in the annular kiln, which has such a comparatively great surplus of air.

When the causes of this inferiority of the annular kiln to the old coal consuming kilns are known, the remedy can easily be applied.

Gages for Pressure and Draft in Furnaces, Gas-Pipes and Air-Pipes.

Another writer has called attention to the importance of regulating the draft in kilns used for the manufacture of ceramic wares.*

Since variations in the pressure and temperature of the atmosphere, and the direction and force of the currents of air retard or accelerate the progress of the fire in the kiln, the draft-gage is designed to enable the burner to regulate the draft by raising or lowering, opening or closing the damper, so that the progress of the fire, based on analyses of the gases, may conform as nearly as possible to normal conditions, and the deficit or surplus of air-supply, which means waste of fuel, be kept within the required limits.

In measuring the atmospheric pressure a U-tube filled with liquid is used, one side of which is connected by means of tubes with the space in which the pressure is to be taken. The difference of level in the two sides of the U-tube indicates the amount by which the pressure exceeds or falls below that of the atmosphere.

If the difference of pressure is slight, as in furnace-flues, gas or air-pipes, the difference of level is very slight, and therefore

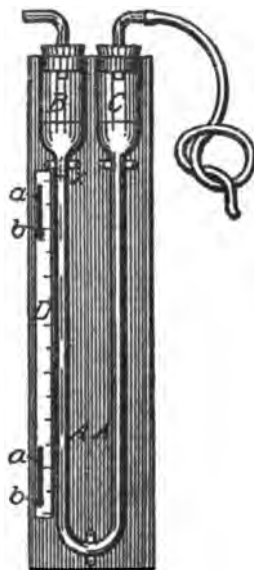
*Notizblatt, 1875, p. 191. "Ein Zugmesser," Dr. Julius Aron.

difficult to measure exactly, especially for an unpracticed observer. But slight differences of level can be measured on an enlarged scale by means of an apparatus illustrated in the accompanying cut.

A U-tube, made of calibrated glass-tubing, terminates at its upper ends in two larger glass tubes of equal size, B and C. The U-tube A B C is attached to a board which carries also a sliding scale D, parallel to one side of the tube, and adjusted by means of the slits a a and screws b b. The U-tube is filled with two immiscible liquids, of about the same specific gravity, in such a way that their point of contact x lies near the zero point of the scale. For example these liquids can be used: water and aniline-oil, or petroleum and diluted alcohol, or carbolic acid and an aqueous carbolic solution. It is well to color one of the liquids.

The apparatus is hung on the wall near the spot where the measurement is to be taken. In measuring a pressure which exceeds that of the atmosphere, the side B, fitted with a stopper and glass tube, is connected with the space in which the pressure is to be measured, but in measuring a lower temperature, the side C is thus connected by means of rubber, glass or metal tubes. The other side is brought into connection with the atmosphere.

When the apparatus has been placed in an upright position and the scale adjusted so that the zero point is opposite the point of contact of the liquids, and one side connected with a furnace-flue, a gas-pipe, or an air-pipe, a slight difference of level is produced in the larger tubes B and C. The difference of level is marked on a larger scale by the shifting of the point of contact of the two immiscible liquids in the narrow tube A, and this difference is in proportion to the diameters of the larger and smaller tubes. For example, if the diameters of the tube A and the tubes B and C are in the ratio 1:20, the lowering of the surface in B one millimeter will cause the point x to sink



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twenty millimeters, so that very slight differences of level are plainly marked.

The division of the scale may be an empirical one, for comparison alone, or, for more exact measurements, it may be given in terms of hydrostatic pressure, in millimeters. In the latter case the divisions can be computed from the ratio of the diameters of A and B and C and the specific gravity of the liquids with which they are filled. The apparatus is more sensitive and exact, the greater the ratio of the diameter of the upper tubes to that of the smaller tube, and the less the difference in the specific gravity of the two liquids.

The following point should be noted in connection with the preparation and use of the apparatus.*

After the stoppers have been removed, the U-tube is filled with the heavier liquid up to the zero point of the scale, and then enough of the lighter liquid is put in, on both sides, to half fill the larger cylindrical tubes B and C. By carefully dropping in the liquid on one side or the other the contact point of the two liquids can easily be made to coincide with the zero-point of the scale.

If a drop of the upper or lower stratum should become separated, it can be united again with the main liquid by cautious suction or blowing through the rubber tube.

In replacing the stopper, the glass tube should be held firmly in place, so that it may not turn, in which case it is likely to break.

Before using the apparatus the scale is adjusted at the zero-point, and it is well to examine now and then whether the zero-point has not been shifted by the evaporation of the liquids. For this purpose the rubber tube is detached from its connection with the kiln, so that both sides of the U-tube are in connection with the atmosphere. If the contact point of the liquids is not exactly at zero, the scale may be slipped along, or, if this is not practicable, a few drops of the liquid may be added on the left side.

It must be stated further that there must always be enough liquid on the left side, so that even if the point of contact of the liquids is drawn to the lowest point, there will still be some of the liquid on the left side in the cylindrical part of the larger tube. This follows from the principle of the apparatus, since,

*The apparatus can be ordered from the Chemical Laboratory for the Clay Industry. Berlin N. W., Kruppstr. 6.

if the larger tube were entirely emptied, only a plain U-tube would remain, and it would not be possible to magnify the depression.

The apparatus is so divided that when the tube is filled, the divisions on the scale give the hydrostatic pressure directly in millimeters.

The Effects of Sulphur in the Coal on Clay Products.

The question has been raised, why is it that the older brick structures in North Germany have successfully defied the inclemency of our northern climate, when it is so difficult at the present time to manufacture bricks which offer such resistance to the weather.

A closer scrutiny of the materials formerly used in making bricks does not reveal any reason for their greater durability. They were generally molded in larger shapes and the difficulties connected with uniform firing were therefore much greater. The fracture does not indicate any better manipulation of the paste than is now possible with our superior mechanical contrivances; on the contrary, there is less homogeneity of structure, and the glazing upon the surface is in many instances a simple, easily fusible lead-glaze, which shows the effects of even slight wear.

On the other hand, many of the face bricks of the present day will certainly prove as durable, if not more so, than the older ones; yet some of them after only a short exposure to the atmosphere show such traces of wear that a permanent resistance to the disintegrating influences of the weather cannot be counted upon.

We may conclude that in former times, as now, inferior materials were often used in the manufacture of bricks, and that only the better ones have come down to us, the poorer material having succumbed to destructive influences in the course of centuries. Still, the opinion commonly held by architects and brick-makers is, that the materials used by the ancients were more capable of resisting climatic conditions than the average bricks of the present day.

The greater resistance of the older materials has been explained on the ground of a better selection of raw materials and a better and more thorough treatment of them. It is said the ancient brickmakers were not only more careful in the selection of clay with reference to its suitability for the manufacture of bricks, but they also dug up the material long before it was to be used, let it freeze thoroughly, turned it over frequently, and allowed it to be leached by the rain and thoroughly decomposed in

the air. This probably was done, and done with a purpose, by the ancient brickmakers, but it is evident that with the help of the resources available at the present time, the structural properties of the raw materials can be even more vigorously dealt with than was possible in former times, and an examination of the older materials confirms this statement.

At any rate, this supposedly better manipulation of the clay cannot be the sole cause of the greater resistance of the older materials.

It is our opinion that the cause of the deterioration of bricks as regards resistance to the weather lies rather in the fact that the firing is now almost invariably accomplished by means of fossil fuel. Peat is rarely used, soft coal oftener, and anthracite coal most frequently, while formerly wood alone was available and was used for this purpose.

It must be admitted that wood is the most convenient and most reliable kind of fuel for the manufacture of all clay products, but it is also the most expensive, and for this reason coal, which is decidedly cheaper, is preferred, except under unusual conditions.

A comparison of the composition of wood and coal will show why the former is better.

From a chemical standpoint wood is a compound of carbon, hydrogen and oxygen, containing only insignificant quantities of inorganic matter, in the form of ashes, the latter consisting usually of potassium carbonate. The hydrogen and oxygen are in nearly the right proportion to form water, so the carbon is really the active essential constituent of the fuel.

On the other hand, in the different kinds of fossil fuel, which originated through the decay of plant life, there are present, in addition to the same organic constituents, carbon, hydrogen and oxygen, considerable quantities of inorganic matter, amounting to 30 or 40 per cent in some kinds of fuel. They are especially injurious, because they are inevitably scattered in the kiln, and also because certain of their elements become volatilized and are absorbed by the clay.

One of the most troublesome of these elements is sulphur, which is present, in its compounds, in the fuel, and passes also into the atmosphere of the kiln. As a rule sulphur occurs in the form of pyrites (bi-sulphide of iron), in brass yellow, shell-shaped deposits, either in the interstices of the coal, or finely distributed and incorporated in the coal. Pyrites commonly occurs in the latter form in brown coal, and in peat.

In the combustion of coal the bi-sulphide of iron is converted into ferric oxide under the influence of the heat and the oxygen of the air, while the sulphur passes into the furnace gases in the form of sulphurous acid. The odor of the gases arising from fossil fuel is sufficient proof of this fact. If oxygen is still present in the furnace gases, the sulphurous acid is oxidized to sulphuric acid by the action of the numerous bases in the clay, such as potassium, sodium, lime, magnesia, and is taken up in this form into the substance of the bricks. This is especially noticeable in the materials which contain the carbonates of lime and magnesia, so that these materials are sometimes completely changed in color by the absorption of sulphuric acid, which is frequently present on the surface to the amount of ten per cent or more.

Under the influence of the protoxide of carbon and the hydrocarbons, which are formed from the fuel whenever perfect combustion is prevented by an insufficient supply of oxygen in the furnace gases, the sulphuric acid absorbed by the bricks is set free again in the form of sulphurous acid and may reach the open air in this form, but from time to time sulphurous acid is supplied to the bricks from the fuel, when the coals burn down and cause a smokeless fire, and so there is again opportunity for the formation of sulphates.

The compounds of sulphuric acid are more readily absorbed into the substance of the bricks, the more easily an excess of air can be admitted to the chambers of the kiln. As a matter of fact, the continuous kilns, which are in general use at present, always do admit an excess of air, unless especial importance is attached to a smoking fire, while in older kilns there is always greater fluctuation in the composition of the furnace-gases, the firing being sometimes smokeless, and at other times accompanied by smoke.

Consequently there is always more reason to fear that sulphates will find their way into the clay when fossil fuel is used, than when wood is used in burning the bricks. Even if the occurrence of such salts in the raw clay is not entirely obviated, nevertheless one cause for the formation of sulphates is removed, and, further, when wood is used, the salts in the clay are more easily and surely broken up, than when coal is used. Therefore there is more probability that these injurious salts are absent in the bricks of recent manufacture than in the old ones.

Let us see how the presence of sulphates in bricks affects their capacity to resist the action of the weather. We cannot assume that there is a chemical action of the salts upon the bricks, but

since they are more or less soluble in water, we may be sure that there is a mechanical action quite like that which ice exerts upon bricks. We may say that as ice breaks up the structure of the bricks by the formation of crystals, so soluble salts have the same effect, since they are precipitated from their solution when the water evaporates.

In this process it is not to be supposed that the salts are deposited as very fine powder upon the surfaces of the bricks, corresponding to the distribution of the solution in the pores of the bricks, but that the tiny particles move from their places, always grouping themselves into single crystals of larger or smaller size, and thereby exerting a pressure upon the adjoining particles. The greater the tendency of the salts to form large crystals, the more readily the disintegration of the bricks takes place. The crystals formed by the sulphates of sodium and magnesium are especially likely to be large, while those of potassium and lime are smaller.

This phenomenon appears anew every time the bricks are moistened and dried, and even though the action of the sulphates is often slight in a single case, owing to the small quantity of the soluble salts, it becomes more pronounced with repeated occurrences.

If the salts are present in the bricks in large quantities, they appear upon the surface. The bricks are then called saltpetre bricks, because it was formerly supposed that saltpetre was formed in them, which is really the case, however, only when organic ingredients are present.

In most cases the salts are compounds of sulphuric acid with potassium, sodium, lime or magnesia. The bases are found in the clay, and the sulphur is largely derived from the coal used in firing.

Disintegration of the bricks takes place very rapidly, of course, when the salts are present in large quantities, and the process is favored when the bricks are exposed to moisture, or when the firing was not very intense; that is, when the structure is somewhat porous.

But a gradual disintegration of the bricks takes place even when the salts are found in small quantities in the pores and do not come to the surface. Such bricks usually withstand the action of the weather for many years, before the disintegration is noticed as it appears first in single bricks, then in greater numbers.

But firing with coal, which always contains some sulphur, the amount varying from the slightest trace to about four per cent of pyrites, has an important influence upon another property of the bricks, besides resistance to the weather, namely, their color. The color which the bricks assume in the firing is frequently due to the sulphur they contain. This is especially noticeable in the materials which contain finely distributed carbonate of lime. If such clays contain a large amount of lime in proportion to the iron oxide, they do not assume the color which iron oxide usually imparts to the clay; that is, yellowish red, reddish brown, or red, but they take on a lighter color, such as flesh color, or yellowish gray. This color is due to the presence of a silicate formed by iron oxide, magnesia, lime and silicic acid.

If the lime is combined with an acid which is not expelled by the silicic acid in the roasting fire, such a silicate cannot be formed, since the lime must then stand aloof from the silicate. In this case only the iron oxide, alumina, and silicic acid combine, and this compound has a dark color, usually red. Now when sulphuric acid is absorbed from the furnace gas, the lime does not form a compound with the silicates of the brick, since lime sulphate is not decomposed by silicic acid or its compounds when the atmosphere in the kiln contains oxygen, therefore the bricks are often red on the surface, but exhibit the normal yellowish color in the fracture and the protected parts. In this case, too, the occasional appearance of smoke in the furnace gases serves to expel again the sulphate which has been formed, since the sulphuric acid is thereby converted into sulphurous acid and is easily expelled in this form. Even if the color is yellow, it usually has a different shade in the spots which were red during the firing, owing to the difference in slagging, so that such spots are somewhat noticeable, especially when the sulphates which were absorbed are not decomposed until a high temperature has been reached, in which case the slagging of the clay is already considerably advanced.

With wood-firing there is no occasion to fear such a discoloration of the clay, because there is no sulphur. When peat, brown coal or anthracite coal is used, the factors which tend to produce discoloration are the presence of sulphur in the fuel, and the impracticability of producing a smoky atmosphere in the kiln.

Experience has shown that it is much more difficult to secure a pure yellow color in bricks in the new continuous kilns than in the older ones with which more waste is connected, and for this reason alone the latter have been retained in many cases.

It is not only the calcareous and yellow-burning clays which show by their color that sulphuric acid has been absorbed from the furnace gases; there are others in which the same phenomenon is observed, even if it is not so marked. Wherever sulphuric acid has once been absorbed, there is a slight difference in the slagging, even though the acid has been driven off again in smoky furnace gases, and consequently a slightly different shade of color is distinguishable in these spots.

In the manufacture of glazes for face bricks and terra cotta products which are to be exposed to the air in facades, the absorption of sulphur compounds into the body of the material is likewise an important factor. It is a matter of common experience that glazed bricks are more easily disintegrated by the action of frost than unglazed bricks of the same quality. This is due to the fact that the ice crystals are hindered by the glaze from passing off from the surface, and in consequence they crowd off the entire glazed surface. To be sure, it is more difficult for water to get into the bricks through the medium of the glaze, but it is by no means impossible. It can always get beneath the glazed surface through flaws in the glaze, which can never be entirely prevented, and through the joints of the bricks.

The crystallization of the ice has the same effect as the crystallization of the sulphates in the bricks, when they are subjected to moisture and subsequent drying; the glaze is pushed off by the crystallization, and the action of the ice in winter is continued in summer by the action of the salts within the bricks.

We cannot suppose that the older glazes were of a different composition, and therefore more durable. A mixture of lead oxide, clay and sand has always been used, and the mixture is made more uniform at the present time, since the ingredients which were formerly measured by quantity are now measured by weight. On the whole, the composition of the ancient and modern glazes must be about the same, for it was just as impossible then as it is now, to fuse glazes containing very refractory silicates or a great amount of alumina upon easily fusible clay material.

Let us now examine the process by which glazed bricks are usually manufactured. The bricks are first burned, usually with anthracite coal; that is, fuel which contains sulphur. They are then sorted out according to color for use as face bricks in facades. The poorly burned and discolored bricks are the very ones which are chosen to be covered with a colored glaze and burned again, for slight defects on their surface will no longer

do any harm. These bricks are of course the first ones to succumb to the action of the weather, on account of the deposit of salts due to the sulphur in the furnace-gas.

Glazes are often burned with wood, but smoke is avoided as much as possible, consequently the salts in the body of the brick are not broken up. Then surprise is expressed when these bricks cast off their glazed coating after a few years!

If the bricks were put through a preliminary firing, also with wood, this would not occur, for in this case the irregularities in color are so great as to make it necessary to select from the charge of the kiln particular bricks for glazing.

It is also probable that it was a general practice formerly, as it is today with wood-firing, not to burn the bricks first, but to cover them with the glaze in their raw condition and burn the glaze on in the same fire with the unglazed bricks, in which case there is much less danger that the body of the brick will absorb salts. This procedure alone is undoubtedly sufficient to account for the undeniably superior resistance of glazed bricks. Brick-makers of the present day should pay more attention to these conditions.

Efflorescences on Terra Cotta Wares.

Of all the annoying phenomena encountered in the attempt to secure an even color in face bricks and terra cotta wares, none are more difficult to contend with than the saline efflorescences which make their appearance during the drying process, in extremely small quantities, on those parts of the molded articles where evaporation takes place most rapidly, that is, on the corners, edges, or projecting parts. The process of manufacture is made particularly difficult and uncertain in result, since these incrustations are usually invisible to the naked eye before the firing, especially in clays which are light colored in their native state.

These efflorescences seem to be more marked the slower the drying process is. Up to the present time this phenomenon has not been studied with sufficient care. Our books on brickmaking contain nothing on the subject. Yet it is of the greatest importance that the matter should receive thorough investigation, for the efflorescences are more likely to appear upon the fine, dense, smooth materials used for the better and more valuable products, than on the sandy, rough-surfaced, porous clays used for the rougher brickwork.

Because the efflorescences are so hard to detect and consequently so little heeded, it has come about that in many plants the failure to secure good colors is laid to the firing, and still the defects are not remedied after years of experimentation, since it is in the drying process that this formation takes place.

Mineral substances are invariably present, in greater or less quantity, in the water used to soften the clay, and the clay itself, especially if it is fat, retains the soluble substances which are formed in the never ending process of disintegration going on in the claybed. If the clay in the bed was exposed to additional weathering through the winter, which is ordinarily necessary for the better products, occasion is often given thereby for the energetic formation of soluble salts, especially if the clay contains pyrites in a finely distributed condition.

The harmful effect of these salts can hardly be neutralized to any great extent, as is often supposed, by leaching through the atmospheric precipitations, partly because clay is rendered absolutely impervious by moistening and leaching is therefore impossible, partly because the formation of salts is not completed until after many years and is made really possible only by freezing, so that the process does not enter upon its most active stage until the clay is in a suitable condition for manufacture.

The removal by rain or snow of the soluble salts formed in the claybed in winter by exposure to the weather can therefore be only a superficial operation. In other industries it has been found impossible to effect on a large scale even a partial removal of soluble salts from those materials which have similar physical properties with clay.

The action of the soluble salts is therefore particularly annoying, since the process of formation is continued during the manipulation and drying of the clay, and because such salty clays are especially inclined to assume upon their surface additional discolored, saline incrustations in the kiln during the drying process.

Since evaporation takes place during the drying process only at the surface, or to less extent at a slight depth, especially in sandy, porous clay, all the moisture must first be drawn to the surface by capillary attraction before it can evaporate, and in this way the salts held in solution approach the surface and remain at a depth varying according to the density of the solution.

After the water has been evaporated, the salts thus expelled take the form either of a dust-like coating or of microscopic

wart-like crystals, almost invisible to the unpractised eye, since they are usually of the same color as the clay, containing, as they do, clayey matter in their scales. They are not plainly distinguishable till after the firing, and then they are of a white, gray or yellowish color and are so firmly burned into the clay that it is difficult to remove them by mechanical or chemical processes.

Many empirical attempts have been made to remove these annoying incrustations, but decided success has been attained in very few instances. Mechanical means have been employed, such as rubbing, brushing, dipping in tar and similar substances, and chemical processes have also been tried. The former are practicable only with special products, and in cases where the incrustation is not very firmly fixed the latter require an accurate knowledge of the chemical composition of the materials in question. Because of the little attention given to the soluble salts in the clay, which is accounted for by the slight quantity in which they appear, the chemical composition of this part of the clay has never received sufficient study, either in practical operations or in scientific analysis, and yet it is of great importance, for the salts cannot be rendered insoluble and harmless unless their quantity and quality are accurately known.

In many cases the efflorescences are said to be formed of gypsum, magnesium, sulphate, carbonate of lime, or magnesia, and such is often the case, at least these substances have always been found in connection with other substances, when a qualitative analysis has been made. However, the analyses given below show that the composition varies, even when the claybeds are in close proximity, and that therefore different means must be employed in removing them.

In the clay used in the Siegersdorf plant in the manufacture of face brick and terra cotta wares, two strata were noticed, one ashy gray, the other blackish in color. Experience had shown that these clays possessed the above mentioned undesirable property, and when the better products were to be manufactured, they were carefully kept separate, even in the pit, from the other clays which exhibited no incrustation. Saline efflorescences were plainly distinguishable on the corners and edges of the pieces of these clays which had been exposed to the air for some time in an unworked condition.

In order to examine these incrustations, a large piece of each clay was boiled with distilled water. After settling, the clear

liquid was evaporated to dryness and the saline mass thus obtained was analysed.

The saline deposit from the gray clay A was crystalline, colored dark by organic matter, and very slightly deliquescent, while that from the blackish clay B was yellowish green, hygroscopic to a high degree, and, when exposed to the moist air, became in a short time a syrup-like liquid.

The composition of these saline deposits was found to be as follows:

| | Gray Clay. A. | Black Clay. B. |
|---|------------------|-------------------|
| Sulphuric acid | 55.13 per cent. | 55.05 per cent. |
| Lime | 11.24 per cent. | Traces. |
| Magnesia | 11.10 per cent. | 4.42 per cent. |
| Ferric oxide with traces of fer- rous oxide | 6.22 per cent. | 32.15 per cent. |
| Alumina | .41 per cent. | 2.16 per cent. |
| Alkalis | 4.82 per cent. | 1.28 per cent. |
| Organic matter | 5.41 per cent. | Traces. |
| Water, chlorine, and undeter- mined substances | 5.67 per cent. | 4.94 per cent. |
| | 100.00 per cent. | 100.00 per cent. |

Accordingly the composition may be calculated in this way:

| | A. | B. |
|--|------------------|------------------|
| Sulphate of lime..... | 27.84 per cent. | Traces. |
| Sulphate of magnesia..... | 33.30 per cent. | 13.26 per cent. |
| Sulphate of ferric oxide..... | 15.55 per cent. | 72.20 per cent. |
| Sulphate of alumina..... | 1.39 per cent. | 7.25 per cent. |
| Sulphate of alkalis..... | 8.82 per cent. | 2.32 per cent. |
| Organic matter | 5.41 per cent. | Traces. |
| Water and undetermined sub- stances | 5.67 per cent. | 4.94 per cent. |
| | 100.00 per cent. | 100.00 per cent. |

It will be seen at once that in A the salts of lime, magnesia, and the alkalis predominate, all of which have a marked tendency to form crystals, which is the real cause of the efflorescences. These salts, therefore, exercise a very harmful influence even in small quantities. In B, on the other hand, the deliquescent salts of iron and alumina predominate, which are not only slow to crystallize, but also prevent the formation of other salts.

These salts have therefore a less injurious effect than the former ones, even though they are present in considerable quantities.

The fact that the soluble salts in the brick were really condensed at the surface was shown by an analytical test of an ordinary brick made of these materials, which when air-dried, showed gray, wart-like crystalline deposits upon its surface. The outer stratum, about .5 mm. in thickness, contained 1.51 per cent of sulphuric acid, the center of the brick only .70 per cent. If the amount of sulphuric acid in the soluble salts of the clay is reckoned as 55 per cent, from the analysis given above, this would mean that the outer stratum, .5 mm. in thickness, contained 2.75 per cent of soluble salts which cause the efflorescence and the center of the brick 1.27 per cent.

At the last general meeting of the association the question of preventing these efflorescences was discussed on the occasion of a paper by Mr. Martin. Since the subject is of such great importance and is in many plants a vital question, I have thought I ought not to withhold this contribution, however little light is shed thereby upon this phenomenon. This much has been shown, however: That a successful attempt to remove efflorescences by a chemical process, by means of empirical experimentation in one place, is by no means an indication that success will be attained in another place. It is also evident that the cost of the process will always be influenced both by the kind and quantity of the ingredients required to precipitate the injurious salts.

Green and Yellow Efflorescences on Face Bricks.

The pleasing shades of color secured from the so-called "brown-coal" clay, which burns yellow, make the use of this clay very desirable in the manufacture of face bricks and terra cotta wares. But these products, after exposure to the weather, often exhibit an ugly deep yellowish green or bluish green efflorescence, which gives place after a time to a dirty brown or blackish color.

The efflorescence seems to be formed most easily when the clay has been only slightly burned, and it does not, as a rule, appear upon all the products of any one burning, but often upon single bricks only. Sometimes it makes its appearance a few days after the bricks have been taken from the kiln, sometimes only after a considerable time, perhaps not until after a winter of exposure to the weather, and not infrequently

its appearance is delayed until the bricks have been set in a facade, to the extreme annoyance of the manufacturer.

The phenomenon is of quite general occurrence, at least in the brick yards which obtain their material from the brown coal deposits of North Germany, which extend from the Oder to the Elbe and even beyond, and traverse the Lausitz and a part of Saxony. Sporadic traces of the phenomenon are found nearly everywhere, and very few plants can boast of entire freedom from it.

Many investigations have been made in the hope of determining the cause of the phenomenon and thus securing some certain means for its removal, but no final or satisfactory solution of the problem has yet been reached. It has been explained as a vegetable growth of lower organisms, an alga which derives its mineral sustenance from the bricks, and undoubtedly this is the source in many cases. In other cases the colored incrustation upon the surface of the clay has decidedly the character of saline efflorescence, and the crystalline or wart like deposit must have a mineral origin.

These efflorescences have often been analysed and reports made in technical journals. In some cases they have been designated as colored salts of metals. Dr. Cohn attributes them to iron salts which were not decomposed in the burning process. (*Thonindustrie Zeitung*, No. 26, 1877). Others have found cobalt compounds, and I succeeded once in determining the presence of chrome compounds as a coloring agent in a red brick covered with a green efflorescence. (*Deutsche Töpfer und Ziegler Zeitung*, No. 34, 1877).

If in the present article I bring forward another metal as the source of the colorations, I do not mean to assert that this metal is the cause of the phenomenon in every case of this kind, but it certainly is in very many instances, and it should therefore be brought to the attention of all who are interested in finding some means to prevent the obnoxious discoloration.

In this case yellow face bricks made of brown coal clay from the vicinity of Wittenberg were analyzed. Incrustations appeared upon the bricks, after they had been exposed to the weather for a time, which covered in some cases the entire surface of the brick and occurred in others only in spots, particularly on the corners and edges. The coating had a golden yellow color which in certain spots changed to a bright yellowish green or grass green. The microscope revealed its structure as a saline, wart-like deposit. Colored coatings of this

sort are to be seen in many brick yards and in all stone quarries. As the shades of color resembled the yellow coloring of chromates and the green shades of chromic salts, I was led to infer the presence of a chrome compound, such as I had discovered on a former occasion. This seemed even more probable when bits of the brick, which were broken off and laid in cold water, imparted a green color to the latter, while the yellow coloring of the brick fragments disappeared completely, and the green color partially. It was plain therefore that the substance was a colored soluble salt. But the original supposition, that the yellow color was caused by chromic acid, proved to be incorrect. It was due rather to the presence of vanadic acid.

Vanadium is one of the rare and therefore infrequently examined metals whose compounds are characterized by very bright and pronounced, but extremely variable colors, since many of its compounds are exceedingly unstable.

The compounds of vanadium in its highest stage of oxidation, vanadic acid, sometimes have a rich yellow color, and are sometimes colorless, but are easily converted by means of reducing agents, such as organic matters or hydrogen sulphide, into the compounds of vanadous acid, the lower stage of oxidation, which are usually aqueous and green or blue, or non-aqueous and brown.

In order to prove the presence of this interesting substance, the colored portions of a large number of face bricks were chipped off with a steel chisel and washed with cold distilled water. The brick powder was removed and the solution evaporated. The color was a deep golden yellow, which disappeared on further heating, but reappeared again on further concentration. When greatly concentrated, the solution assumed a deep grass green color, and after it was completely dried a bluish green deliquescent salty mass was left, which showed again the grass green color on being dissolved with water and dilute sulphuric acid.

From this salty paste, in which the presence of vanadium was proved beyond a doubt by means of the blow-pipe, pure vanadic acid was secured according to the directions given by Rose (*Handbuch der analytischen Chemie*. 1871, pp. 364, 368). For this purpose the saline paste was dissolved in nitric acid, and from this green solution the vanadic compounds were precipitated in the form of a chocolate brown powder by means of barium chloride and ammonia. This powder was washed,

dried and dissolved in hot concentrated sulphuric acid and then poured into enough cold water to precipitate the sulphate of baryta. The resulting solution of vanadic and vanadous acid in sulphuric acid showed the color of a copper-vitriol solution. The solution was freed from sulphuric acid by evaporation, and oxidized with nitric acid, and thus vanadic acid was obtained in the form of a red molten paste with all the characteristic reactions of vanadic acid. For further details of this experiment the reader is referred to Rose's Handbook of Analytical Chemistry.

It has long been known that vanadium occurs not only in iron ores, in very small quantities however, but in many clays also. But it does not seem to be generally known that it occurs in soluble compounds in burned clay. Since it is present in such small quantities it escapes notice entirely in the ordinary analysis. But since the compounds of vanadium possess a very extraordinary capacity to impart color, very striking phenomena may be caused by its presence, even in the most minute quantities, as we see in this case.

Since the colored efflorescences do not appear upon all the products of any one burning, but only upon single bricks, it is reasonable to suppose that the manner of burning, or the character of the furnace gases determines whether the compounds of vanadium present in the clay will appear as soluble or insoluble salts in the burned products. Further experimentation is necessary to discover what influences produce the one effect or the other.

The Compounds of Vanadium in Brown-Coal Clay and the Green and Yellow Colors Which They Cause in Terra Cotta Products.

In the preceding chapter I have suggested compounds of vanadium as the cause of the unsightly green or yellow efflorescence which frequently appears upon the products manufactured from the brown-coal clay of North Germany soon after the firing, or after they have been set in facades. These compounds of vanadium can be separated from the clay after it is fired, in the form of soluble salts. After the moist wares are dried the surface is disfigured by the appearance of this wart-like crystalline efflorescence.

As this phenomenon is of very general occurrence, we have here a foe to the brick industry to contend with, whose very presence has been hitherto unsuspected. However, the dis-

covery of the cause of the trouble puts us in a position to find means to obviate it.

After the qualitative test which disclosed the presence of the coloring compounds of vanadium, the first point to be determined was, in what form and in what quantities these compounds are present in the clay after firing, and also what substances accompany them, in order to gain a starting point for the method to be adopted in getting rid of the trouble. For this purpose more detailed experiments were made.

The first step was to procure sufficiently large quantities of this interesting green coloring substance for the experiment. The material which I used was secured from face brick covered with the efflorescence, furnished me by the proprietor of clay works on the Elbe.

Pieces of the brick of not more than 1 cm. in thickness were covered with distilled water, which was poured off at the end of 24 hours, and was then renewed whenever it showed a decidedly yellow color. This was done six times. The golden yellow liquid was clarified from the brick powder and then evaporated to dryness in a large platinum dish. At a high stage of concentration little orange-red crystals were separated from the yellowish green liquid on cooling. When dried they appeared as a brownish green salty mass, which became siskin green after pulverization.

In this way 2.3995 gr. of the salty mass containing vanadium were obtained from 1550 gr. of brick powder, that is .155 per cent.

The composition of this salty mass which must be identical with the green or yellow coloring substance which appears upon brick facades, was as follows, according to the chemical analysis:

| | | |
|-----------------------------|-------|----------|
| Potassium | 19.82 | per cent |
| Sodium | 3.17 | " " * |
| Lime | 3.24 | " " |
| Magnesia | 3.34 | " " |
| Alumina and iron oxide..... | .77 | " " |
| Vanadic acid | 29.43 | " " ** |
| Molybdic acid | 1.12 | " " |
| Sulphuric acid .. | 15.70 | " " , ** |
| Silicic acid | 2.07 | " " |
| Chlorine | 2.63 | " " ** |
| Water | 18.25 | " " |
| Insoluble matter | .46 | " " |

* Remainder. 100.00 per cent

** The mean of two weighings which agreed very nearly.

After the alkaline clay and the alumina had been removed by means of sodium carbonate, the vanadic acid was precipitated by means of ammonium chloride in the form of ammonium vanadate, and from the acidified filtrate molybdenum was secured by means of hydrogen sulphide as molybdic sulphide.

If the acids are distributed among the basic substances the salt mixture may be regarded as containing:

| | | |
|--------------------------|-------|----------|
| Potassium vanadate | 44.38 | per cent |
| Potassium sulphate | 9.01 | " " |
| Lime sulphate | 7.97 | " " |
| Magnesium sulphate | 10.02 | " " |
| Sodium molybdate | 1.62 | " " |
| Common salt | 4.47 | " " |
| Soluble silicates | 3.82 | " " |
| Water | 18.25 | " " |
| Insoluble matter | .46 | " " |

100.00 per cent

It appears, therefore, that the efflorescence consists mainly of potassium vanadate, which is accompanied by the substances which usually form saline efflorescences upon masonry, gypsum, magnesium sulphate, alkaline sulphates and common salt.

It is of interest to note the appearance, although in small quantities, of molybdic acid, a compound of molybdenum, a metal of rare occurrence, which is closely related to vanadium in its properties, and like the latter has a very deep color in its compounds.

Vanadium, a gray metal, difficult to fuse, forms three compounds with oxygen, which may be present in the clay.

1. Vanadous oxide (65.55 vanadium + 8 oxygen). This is black and forms soluble compounds.

2. Vanadic oxide (68.55 vanadium + 16 oxygen). The salts, which are mostly soluble, are blue or green.

3. Vanadic acid (68.55 vanadium + 24 oxygen). All the salts are soluble and are bright yellow.

The coloring power of the vanadates is so extraordinarily great, that it can be recognized, when all other means for the detection of vanadic acid fail.

Besides the compounds mentioned there are also compounds of the two latter compounds, that is, vanadates of vanadic oxide, which have a deep green color, are partly soluble in

water, and possess likewise marked coloring power. They are formed from the compounds of vanadic acid when they come in contact with reducing substances, such as dust, organic matter, hydrogen sulphide, etc.

The compounds of molybdic oxide, which correspond to vanadic oxide in composition, are blue or crimson, those of molybdic acid are colorless. The molybdate of vanadic oxide and also the vanadate of molybdic oxide are likewise green.

In these materials we have therefore beyond a doubt the color phenomena under discussion. The experience of manufacturers confirms this conclusion entirely, for the salts, which are at first yellow, are converted into the green or blue compounds by dust, impurities in the water, soot, or gases arising from decay.

The colors are so characteristic of the salts that anyone who has once become familiar with them in any material will recognize them at once. These colors can be seen in nearly all facades, brick plants, and tile factories, where brown-coal clay is the material used. I do not know of a single plant which uses as raw material the brown-coal clay so common in North Germany, where this trouble does not occur at least occasionally, and in most of them it is very conspicuous.

From the standpoint of the brick manufacturer it might be said: It is extremely interesting to discover that we are dealing every day with a material in our bricks which up to this time has been considered one of the rarest, which only a few chemists have ever seen, and still fewer been able to study, which now appears to be of very general distribution, even though it does occur in small quantities—but of what practical use, of what financial value, is this discovery?

Unfortunately I am not able now to give the ways and means of attacking successfully this foe to the brick industry, for the properties of the compounds of vanadium have been less thoroughly investigated than those of the metals of more frequent occurrence, and it is difficult at present to determine how to render them harmless.

But at any rate when the cause has been discovered, an opportunity is afforded for study in a definite direction. I shall, however, not fail to state as fully as is possible at the present time my views as to the means which should be employed in practical operation, and shall report the experiments I have tried along this line.

It is not to be assumed that the reason why the compounds

of vanadium, of whatever kind, appear on single bricks and not on all, is that they are sporadically mixed in with the clay, as it is worked up. It is more natural to suppose that they form an element common to all brown-coal clays of the North German plains. The more or less marked character of the green efflorescence is probably due, not to any difference in the clay strata, but rather to inequalities in the firing, since no selection of the raw material is made, and the wares in different parts of the kiln differ in the tendency to take on the efflorescence.

In the plant mentioned above, face bricks which become green are found particularly in the back part of the partially annular kilns in use there, while those in the front part are usually quite free from efflorescence, and in general it is only the less thoroughly burned products which are covered with an efflorescence. Since we cannot assume that the clay containing vanadium gets only into the back part of the kiln, the appearance or non-appearance of the efflorescence must be due to the firing.

Since vanadium in its lower stages of oxidation can always be converted into compounds of vanadic acid by heating in the presence of air, we must look upon the admission of air as the primary cause for the formation of this compound which imparts such a decided color. In fact, when the clay under discussion, taken from any raw face brick at random, was heated in a dark red glow with access of air and then covered with water, the water took on a distinctly golden yellow color. This yellow color appeared also when the clay was burned in test kilns, in the form of little sample bricks, and the temperature was raised to a point between the melting point of silver and copper, i. e., 960° — 1100° C.

By means of reducing agents, such as hydrogen, hydrocarbons, carbon dioxide, etc., which are easily formed during the firing, and are always present in the kiln, all compounds of vanadic acid and vanadic oxides are easily converted into vanadous oxide, the only insoluble compound, which likewise is changed to vanadic acid when air is present.

The attempt was made to conduct the test firings in such a way that the unburned combustible gases should at times be in excess in the kiln, in order to fix the coloring compounds of vanadium in the form of vanadous oxide by slagging. The result was that the clay which had been softened with a highly colored solution of vanadic acid, in order to magnify

the phenomenon, and put in water after the firing, imparted a decided yellow color to the water when the temperature of the firing was low, below the melting point of silver, 960 deg. C., but produced a scarcely perceptible color when the temperature was raised to the beginning of a white glow, and the clay began to slag.

From this experiment it seems that during the cooling process, which is always carried on in an atmosphere containing oxygen, in order to secure pure colors in the bricks, the vanadous oxide is changed again into vanadic acid, and the only conditions under which this change does not take place are those existing when the process of slagging has commenced and has fused the lower oxide of vanadium with the volatile silicates.

It rests with the manufacturers of kilns and the practical burners to create these conditions in the firing, and it is evident that this is possible and that the conditions are often present without any effort from the fact that certain firings or certain parts of the contents of the kiln are entirely free from the efflorescence.

The Peculiar Action of Quartz Sand in Brick Clay.

Several years ago I had an opportunity to study on the field of practical operations the difficulties which arise from the changes in the process of manufacture made necessary by diversities in the raw material, and also to observe what unforeseen obstacles may result from an imperfect acquaintance with the properties of the clay.

Occasion for a detailed discussion of this subject is offered in the published report of C. Holthof* upon a brick clay which exhibited very peculiar properties when burned in an annular kiln. A review of this report will certainly be of interest, as similar sensitive materials are used elsewhere.

The manufacture of bricks is an extensive industry in the vicinity of Havre, in France. Two widely differing kinds of clay are used there, furnishing products of entirely different nature.

The Seine widens out into a bay, as it were, and from either bank rises a plateau with elevations of fifty to one hundred

*Notizblatt des Deutschen Vereins für Fabrikation von Ziegeln. No. 3. 1877.

meters, in which are found deposits of highly ferruginous clay mixed with coarse-grained sand. From this clay blackish blue clinkers are manufactured, similar to those of Oldenburg. They are used not only in the extensive hydraulic works of this great seaport, but are also exported in large quantities to Norway, as a return cargo for the imported wood.

In the lowlands at the mouth of the Seine there are extensive deposits of mud saturated with salt water. They must have been raised up out of the sea in comparatively recent times, for the tide is said to have risen at the beginning of the present century up to the spot where a considerable number of large brick yards are now standing.

The most distinctive property of this material is its extreme fineness. It is, however, very short, not bonding easily, and exhibits in high degree the properties of "sluff," fine-grained, imperfectly weathered mineral residue; that is, it becomes stiff when lying undisturbed, but is rendered quite soft by pressure and kneading.

From this material bricks are molded in sanded molds in the Flemish style. The large open kilns in which they are burned contain 200 to 250 thousands of the little French shapes. The fuel used is crushed anthracite coal. These yellow bricks are very light and friable, but are capable of resisting the mild climate of Havre, and are therefore used in the brick work which is almost exclusively employed in buildings there.

It is evident that the clay is very sensitive to changes of temperature in burning, for in the older kilns the lower six or eight courses are always cracked and almost worthless.

Since the annular kiln had been used with great success in burning the blue clinkers, while the loss attendant upon the manufacture of these yellow bricks was so very great, a large annular kiln was erected for the burning of the latter product.

The first burnings were entirely satisfactory so long as the annular kiln was damp, but deteriorated whenever it was dry and the firing was more rapid, so that the proportion of good uncracked bricks sank to five or ten per cent, a showing unparalleled in any other annular kiln.

An investigation of this remarkable phenomenon was begun at once. When examined under the microscope the clay was found to consist in great part of very small splintery and rounded particles of quartz mixed with numerous calcareous shells and branch-like fossils of siliceous infusoria. Further

examination by means of washing and chemical analysis showed that it contained only about 16 per cent of clay, in grains of less than .01 millimeters diameter, and 31.3 per cent of carbonate of lime, besides the fine quartz dust and other mineral residue.

Owing to the great amount of quartz, which expands after the red heat is reached, the clay did not shrink in burning, but on the contrary increased about 1 per cent in length.

The slight bond, the open structure arising from the large admixture of carbonate of lime and infusorial earth, and the tendency of the quartz powder to expand when heated, thus producing a tension within, were perhaps the causes of the great sensitiveness of the clay during the burning. The phenomena which were observed corresponded entirely with this assumption.

In view of the presence of a large amount of lime, it might be supposed that the latter would absorb water and produce a bursting of the brick after the firing, but, if that were the case, the phenomenon would have been more marked while the annular kiln was damp. Furthermore, the bricks underwent no further injury, even after standing a long time in the open air, and it was noticed also that the injury to the bricks had already taken place before the full heat was reached. It is clear, therefore, that the expansion of the lime is not responsible for the damage.

The nature of the injury may be described as follows: an irregular network of cracks appeared, especially upon the faces of the brick turned toward the draft. The cracks extend from one to two centimeters into the heart of the brick and became wider as the clay was burned harder, reaching sometimes a width of five millimeters. The core was usually uninjured, so that the bricks had the appearance of being swollen. Yet they still had a good ring.

In order to determine in what stage of the burning the injury to the bricks took place, some of the bricks were drawn out with tongs through the fire holes during the burning and were examined with a microscope after they had cooled. It was found that cracks became visible as soon as the bricks had reached a dark red heat and could be multiplied to a network of veins by blowing upon the surface while this condition existed. On the other hand, the bricks which had come into the bright red heat, and showed by their yellow color that fusion had begun, were quite indifferent to the

rapid cooling. This shows that the clay was in a state of tension at that stage in the burning when the quartz dust, which was present in large quantities, began to expand, while the bonding substance, the clay and carbonate of lime were not yet softened.

In the older kilns of primitive construction the change of temperature affects only the bricks in the lower part of the kiln, but in this case the same effect is produced at each row of fire holes when fresh fuel is put in, as the strong current of air strikes the bricks at the very time when they are most sensitive to changes of temperature, that is, in the light firing.

The difficulty was somewhat lessened, though not entirely obviated, by decreasing the draft, carefully closing the fire boxes, and diminishing the size of the fire holes by inserting iron funnels with a small opening which allowed only the powdered coal to fall through. A complete remedy was obtained only when the clay was mixed with one-tenth to one-fifth fat clay, in order to increase the bonding power of the former.

This interesting clay has been carefully studied by C. Holthof, and the following statistics are taken from his reports, which cover the chemical changes undergone by the clay by reason of the absence of carbonate of lime during the burning.

The fine grained paste of slight bonding power, in which large bits of shell were often present, was first subjected to careful washing with the Schön apparatus. The quantity passing through varied as follows, according to the velocity of the rising stream of water:

Between .10 and .18 mm. = 24.9 per cent.

Between .18 and .48 mm. = 10.4 per cent.

Between .48 and .99 mm. = 6.8 per cent.

Unwashable at .99 mm. = 56.4 per cent.

Unstable through a sieve of .2 mm. mesh = 1.5 per cent.

On examining these figures one is surprised at the small amount of paste, the real clay material, which can be washed out when the stream has its least velocity.

All the products of the washing effervesced when covered with hydrochloric acid, which showed that they all contained carbonate of lime. When examined under the microscope they were seen to consist partly of the shells of mollusca and infusoria.

The fine average powder was now subjected to a rational analysis. It was first treated with hydrochloric acid, in order to remove the carbonate of lime, and then heated for eighteen hours with sulphuric acid. The result was as follows for the powder dried at 125 deg., which had shrunk about 1.92 per cent as compared with the air dried paste:

| | |
|---|---------|
| Undecomposable residue, sand..... | = 47.88 |
| Chemically combined silica..... | = 8.89 |
| Alumina | = 3.71 |
| Ferric oxide | = 1.28 |
| Ferrous oxide | = .86 |
| Lime | = 17.91 |
| Magnesia | = 1.28 |
| Potassium | = .68 |
| Sodium | = .17 |
| Phosphoric acid | = .16 |
| Sulphuric acid | = .406 |
| Carbonic acid | = 14.39 |
| Chemically combined water and inorganic matter... | = 2.88 |
| | <hr/> |
| | 100.00 |

From these figures the composition of the paste may be determined. Aside from a small amount, .5 per cent, of carbonate of ferrous oxide, or carbonate of magnesia, .10 per cent of gypsum, and .36 per cent of lime phosphate, there was found:

46 per cent of quartz sand and residue of primitive rocks,
e. g., feldspar, mica, etc.;

31 per cent of carbonate of lime, in the form of marine
animals;

12 per cent of alumina. (See footnote, page 282.)

9 per cent of minerals soluble in sulphuric acid, together
with organic matter.

The sand was analyzed again after its separation, with the
following result:

| | |
|---|-----------------|
| Silica | 94.14 per cent |
| Alumina and traces of ferric oxide..... | 3.25 per cent |
| Lime | .23 per cent |
| Magnesia | .20 per cent |
| Potassium | .99 per cent |
| Sodium | 1.90 per cent |
| | <hr/> |
| | 100.00 per cent |

It is clear from this analysis that the paste contains large quantities of quartz, and that the well known tendency of this mineral to expand when heated is the cause of the expansion of the bricks in the fire.

In order to determine the chemical reaction which takes place when the paste is burned, a brick made of this material and burned in a kiln here was analyzed, with the following result:

It contained in unburned matter:

48.91 per cent insoluble residue,

9.6 per cent silica soluble in water.

These figures coincide very nearly with the 47.88 per cent of insoluble sand, and 8.89 per cent of chemically combined silica given in the analysis above, and fall entirely within the limits between which the results of analyses always vary, even when the subject is entirely homogeneous matter, unless it is exactly the same average powder which is under analysis.

It is evident that only the silica present in the material and soluble in sulphuric acid has entered into composition with the lime and actually remained unchanged in the paste when the quartz sand was heated.

On the other hand, the silica of the clay has become soluble in hydrochloric acid, and has bonded a part of the lime present as well as the alumina.*

A large part of the latter, however, has remained free in the form of caustic potash and this may be the cause of the cracking of burned bricks which has often been observed.

If some clay richer in alumina were mixed with this material, there is no doubt that this difficulty would be obviated, since in the burning the free lime unites with the silica and also with the alumina of the clay, and the colored brick will no longer contain free lime.

*Assuming that the ferric oxide was present in the clay in the place of equivalent quantities of alumina, and that the chemically combined water was not partly represented by equivalent quantities of ferrous oxide, lime, magnesia, potassium, or sodium, the result was:

4.94 per cent alumina and ferric oxide combined,

5.37 per cent silica,

1.65 per cent water,

that is 11.96 per cent real clay material.

The experiments made in the laboratory show that the union of the constituents of the clay with lime takes place at a low temperature and is more complete than the union even of amorphous silica with lime. It is an interesting fact that although the clay is a basic silicate, it combines with the bases at a high temperature, e. g., with the fixed alkalis, lime and magnesia, and breaks up even the more easily destructible compounds of these bases with acids. In this process double silicates are apparently formed, in which the base has taken the place of the water.

This property of the hydrosilicate of alumina is best shown in its action upon the nitrates of potassium and sodium. At a temperature below the fusing point of lead the clay decomposes sulphuric acid with more violence than any other substance except amorphous silica in a red heat.

If the excess of nitrates is removed with water, it is seen that no soluble silicate of potassium or sodium was formed, but that a compound of the clay with potassium or sodium was formed, not readily soluble in water, but easily broken up with dilute acids, the analysis of which shows that the constitutional water of the clay is more or less displaced by potassium or sodium, according to the length of the experiment and the height of the fusing temperature.

The clay also decomposes easily other compounds which are broken up by free silica, although the effect is not so marked as in this case. Thus sulphate of lime is decomposed by the clay, even in a weak reducing fire, at a lower temperature than by silica. Probably therefore the clay in the materials used to make bright-colored face bricks is subjected to an especially favorable influence for the production of pure colors.

The Admixture of the Compounds of Barium with Clay in the Manufacture of Face Bricks.

The green efflorescence upon face bricks caused by the compounds of vanadium can be prevented by very hard burning, ending in a reducing fire. The light white coating which often appears upon the surface during the drying process may be avoided by mixing with the clay a small quantity of native carbonate of barium (witherite). The same end has been attained of late years by the use of barium chloride, which can now be obtained at a reasonable price.

It seems to me desirable to set forth clearly the action of the compounds of barium upon clay.

When the water which is contained in the pores of the clay and gives the latter its plasticity, holds salts in solution, white exudations always appear upon the surfaces of face bricks.

During the first part of the drying process this water evaporates from the surface of the bricks alone. The salts held in solution are deposited in the form of minute crystals, while the water is continually being drawn to the surface by the capillary action of the clay.

The action of the salts differs according to their nature. The sulphates of lime, magnesia, alumina, ferric oxide, and sodium are the principal salts which are found in clay in large quantities. Their chlorides or phosphates, or the compounds of their oxides with the acids arising from the decay of organic matter are usually found in smaller quantities, and are generally known as crenates, or pit-salts.

The most harmful of these salts are the sulphates of lime, magnesia, and sodium, because they crystallize readily upon evaporation. The chlorides are less harmful, as they remain in a state of solution in a very small quantity of water, and also because they are themselves deliquescent in part, so that they do not assume a solid form in a moist atmosphere like that of the drying sheds. The sulphate of lime is especially dreaded, because it is the first of all the salts to crystallize, its solubility being one part to 450 parts of water.

But it is not only the sulphates in the clay which cause an efflorescence upon face bricks.

The water used to moisten the clay in making the mud usually contains salts in considerable quantity; in fact, it is frequently a saturated solution of lime sulphate, so that this also must be taken into account. It has been observed in practice that very small quantities of lime sulphate produce a discolored efflorescence upon bricks and, when as little as 0.1 per cent is present, extremely unsightly discolorations appear upon the surface.

Let us examine the action of barium compounds in admixture with clay upon these salts, taking up first barium carbonate.

Barium unites vigorously with sulphuric acid, forming a compound absolutely insoluble in water. It therefore withdraws the sulphuric acid from the lime sulphate, magnesia, alumina, ferric oxide, and in part from the sodium, and con-

sequently these bases likewise form insoluble carbonates, or hydroxides.

Therefore, since the soluble sulphates, together with the bases, are completely removed from the water with which the brick is filled, no further efflorescence of these salts can take place.

An excess of insoluble barium carbonate is not injurious. It is unavoidable, for the mixture of the clay with barium carbonate can never be so complete that the latter can have perfect action, and the compound is not formed so rapidly, that the sulphates can with certainty be rendered completely insoluble, when merely the necessary amount of barium carbonate is used.

When lime sulphate is contained in the clay to the amount of .1 per cent, only .127 per cent of barium carbonate is needed to decompose it, but generally about 2 per cent of native barium carbonate, or witherite, is used. If the finely pulverized artificial preparation is used, which is more expensive, a smaller quantity is sufficient.

If barium chloride is mixed with the clay, a considerably smaller quantity may and should be employed. Barium chloride is readily soluble in water, and, when dissolved, is easily transmitted to all parts of the clay and begins its action immediately. But more care must be taken here.

Barium chloride precipitates all the sulphuric acid, but in its place there appear soluble compounds of calcium chloride, magnesium chloride, and aluminum chloride compounds, which, being easily soluble, will appear later as an efflorescence upon the surface, but should not be allowed to occur in large quantities.

An excess of barium chloride should likewise be avoided, since it may also reach the surface and make its presence known after the burning by its partial decomposition and the formation of barium silicate. In such a case it is always necessary to determine in advance, by analysis, the proper amount of barium chloride in the clay and the water used to moisten it, in order to avoid an excess.

For .1 per cent of lime sulphate, or other sulphates, in the clay and water, only .17 per cent of crystallized barium chloride is needed. If used in excess, it has the same action as lime sulphate, though not so violent.

This method is not especially to be recommended, on account of the preliminary analysis, and the varying quantities

of sulphates in the clay and water, still, when the sulphates are present in small quantities, it is not without advantages on account of its cheapness.

If there is much lime sulphate present in the clay, not only in solution, but also in larger crystals, in the form of mica, a large quantity of barium chloride is often required to decompose it. The readily soluble chlorides will therefore be greatly increased in quantity, and the very purpose for which the admixture was used, i. e., to prevent efflorescence in drying, will be defeated.

In such cases it is better to use the barium in the form of barium carbonate, because then only a small part of the lime sulphate, viz., only that dissolved in water, but not that present in the clay in stable form, can exert any action. Moreover, since an excess of barium carbonate is needed here, it will not always be necessary to take into account the gypsum in the mixing water, which often varies in amount according to the season.

It is not to be expected that the admixture of any other preparation of barium will have any effect upon the separation of other salts than sulphates, however, efflorescences are much less likely to result from other salts.

As a rule the compounds of barium do not act at all upon the efflorescences which the furnace gases may produce during the burning, if the watersmoking is not carefully attended to.

The action of the sulphuric acid, which is formed from the sulphur in the furnace gases, affects at first only the surface of the brick, not the heart, and besides it is usually present in such large quantities that the small amount of the barium compounds in the clay will exert no appreciable influence.

Thus the barium acts only upon the salts present in the clay during the drying process, and only upon their sulphates.

**The Density of Clay After Molding, Pressing and Drying, and
the Effect of Its Composition Upon the
Density of the Mud.**

In the manufacture of many kinds of clay products it is of prime importance to secure uniformity of shape and size in the individual pieces, especially when these are to be set in a surface with uniform or close joints, e. g., in walls, floors, and pavements.

The manufacturer is confronted here with a difficult problem, for the material he has to deal with is different from other materials in that the single pieces cannot be shaped directly by molding into the desired form, but are always subject to changes in dimension, and partly in form also, during the process of manufacture. He is practically helpless in the face of this difficulty if a definite standard is insisted upon, for the changes which take place are not constant enough to enable him to see the result of his work in advance.

The cause of the difficulty in this case is the tendency of the clay to expand when mixed with water, and to shrink again when the water is evaporated.

Besides the shrinkage of the clay, there are other influences which may produce a distortion of form during the drying process. These may, however, be prevented to some extent in well constructed plants, by securing a degree of stiffness in the clay suited to the shape and weight of the products, so that they will not undergo malformation by reason of their own weight, and further by taking precautions to avoid rapid, uneven drying, which causes warping or cracking.

However, when all these obstacles have been met, there still remain difficulties in preserving the shape and dimension of the products in the burning which follows.

Every clay object contains, when dried, pores which vary in number according to the composition and fineness of the mud, and the manner of molding. In the first stages of the burning these pores are increased in number by the evaporation of certain constituents of the clay, especially the chemically combined water and organic matter, and carbonic acid, in case the clay contains lime. The object in burning the clay is not only to destroy its capacity to become soft by absorbing water again, which can be accomplished only by the removal of the chemically combined water, but also to condense and harden it by partial fusion, so that it will resist the action of the weather or mechanical wear.

The highest degree of resistance to these influences is secured in clay products when the pores of the clay are closed by thorough fusion, making it impervious to water, and when the separate constituents are so thoroughly fused with one another that the fracture presents the appearance of glass or stone. This degree of fusion is always demanded in porcelain, earthenware and those clay products which are subject to hard

mechanical wear, such as paving bricks, floor tiles and artificial paving stones.

In all these products the shrinkage in burning must correspond in general to the extent of space in the pores in the first stage of the burning. It is clear, therefore, that the difficulty of preserving definite dimensions after the burning corresponds to the extent of the shrinkage processes just named, i. e., to the amount of water needed to wet the clay for molding, and the porosity of the clay after drying, or after the evaporation of certain constituents in the first part of the burning, upon whose relation to the outer dimensions of the products the shrinkage in burning depends, when the temperature is increased until the pores are fully closed.

The effect of the shrinkage from drying upon the clay products can at the outset be controlled to a certain extent, and throughout the drying process there are opportunities to make corrections in form.

This may be accomplished by covering the wares which are especially liable to distortion with moist clay or cloths, in order that the parts from which evaporation takes place less rapidly may be kept in the same condition with the others. Or the same result may be secured after the period of most rapid shrinkage, or while the clay still has a little plasticity, by repressing, or by using a wooden heater, to correct any distortions of form which have made their appearance at this point.

The defects which appear during the drying process cause a loss only of the labor in molding and drying, as the material itself can be used again, but this is not the case with the shrinkage in burning. The latter can neither be checked nor controlled, and involves a loss not only of all the previous labor, but also of the material and fuel, since the products thus distorted are likely to be entirely worthless or at least of very inferior quality. The object of the manufacturer should therefore be both to reduce as much as possible the shrinkage in drying, and to secure the greatest density in the clay after drying, because the shrinkage from burning can only be reduced when the density is as great as possible.

Two methods of reducing or preventing the shrinkage in drying seem practicable. The first is, to diminish the amount of water with which the clay is softened in molding, the second to give up entirely the advantages arising from the plastic properties of the clay, and, in cases where the form of the de-

sired products admits it, make use of dry powdered clay, employing great mechanical force to reduce it to a compact mass.

Both methods have been employed in large establishments, With the latter the form of the products has been preserved very successfully up to the beginning of the burning, but there is great difference of opinion as to which method produces objects which will preserve their shape best in burning, where complete fusion of the mud is desired, i. e., those which are most dense before burning and therefore least subject to shrinkage.

Since no exact experiments have been made up to the present time, it may be of general interest if I present the results of some investigations which I have made along this line.

The two kinds of clay which were used for the experiments are found in North Germany, in Heegermühle, near the Finow canal. They have the same chemical and physical properties and are used in the manufacture of clinkers. One is a calcereous, diluvial clay, and is used in the manufacture of yellow bricks for mason work and facings. At a temperature above the melting point of gold, these are converted under great shrinkage into green clinkers.

The other clay contains little lime, but much iron. It is found deposited above the former clay. It is burned at a lower temperature than this one, and with less shrinkage produces dark reddish brown clinkers, which wear better. Both kinds of clay were carefully washed before using. The tables at the close of this article show the density of each clay alone and also of the mixtures of each with the other and with powdered clinker brick clay in the form of terra cotta and quartz sand, both in kernels up to 1 mm. in diameter.

Both kinds of clay and also their mixtures were thoroughly dried and powdered and pressed into blocks 15 cm. square and 1.5 cm. thick. The press used was the hydraulic press of the Royal Porcelain Factory, which is used in making flagstones.

These blocks were divided by three cuttings into six approximately equal parts, the surfaces were neatly trimmed to prevent crumbling and three parts of each were laid aside for a test of porosity in drying and burning. The other three parts were softened in water, and, from these, by means of simple pressure and molding, little bricks were made in a bronze mold in length 6.6 cm., in breadth 3.3 cm., in thickness 1.5 cm.

Half of these were dried at once in the air, the other half,

which had about the consistency of leather, was re-pressed in the bronze mold by means of a few light blows of the hammer upon a stamp which covered it, until the edges were perfectly sharp.

Besides this, a part of the red burning clay was spread out thinly and laid in the cellar for several days. In this time it absorbed 9.5 per cent water from the air, so that it felt clammy and could be balled a little in the hand. From this material more blocks were formed in the hydraulic press, once under full pressure, and a second time with application of the larger air pump alone.

The porosity of the two kinds of clay molded under such different conditions was determined by direct measurement of both raw and burned samples, that is, by measuring the external volume and also the quantity of some indifferent liquid with which the clay was saturated.

For the unburned clay non-volatile petroleum was used with a specific gravity of .805. This was obtained by separating the lighter oils from the ordinary petroleum by means of steaming until the boiling point reached 180 degrees C. The brown residue was deprived of its color by shaking with concentrated sulphuric acid and caustic soda and appeared as an almost odorless liquid, clear as water, with bluish opal tints and was quite indifferent toward the unburned clay.

In order to determine the porosity of the burned samples they were saturated with water. To make sure that all the air bubbles were removed, they were first saturated with alcohol, then plunged into boiling water, in which they were boiled for some time until the alcohol was entirely evaporated, and were finally allowed to cool in the water.

The exterior volume of the bricks was measured by an apparatus constructed for the purpose, which is represented in the accompanying cut. It consists of a glass bottle A containing about one liter. In one side, near the bottom, there is a glass faucet, and above this an opening which is placed in connection with a graduated tube containing 50 to 60 cubic centimeters, with divisions of $1/10$ cu. cm. The neck of the bottle C through which the samples of brick are introduced has a diameter of 5 or 6 cm. and is closed by means of a well-ground glass stopper, hollow on the under side. Through a hole in the stopper a thin glass tube is inserted which terminates at the top in an open bulb. Upon this tube a notch is cut at the same level with the zero point of the graduated tube.



Upon the upper end of the graduated tube, which has a thin, straight opening, a rubber tube is attached, which can be closed by a stop cock.

In order to measure the external dimensions of a clay object, the apparatus is first filled with boiled water, or with non-volatile petroleum, if the objects are unburned, until the liquid reaches the zero point in the tubes a and b. If air bubbles appear, they may be collected in the hollow of the glass stopper by tipping the apparatus, and then removed through the tube b. The liquid is introduced through the tube b and removed through the faucet in the side. When the apparatus has been adjusted, suction is applied to the rubber tube until the graduated tube a is filled to the top and kept filled by closing the stop-cock. Then the wide neck c is opened and the brick, which has previously been saturated with water or petroleum and dried on the outside, is put in. The neck c is now closed, the stop-cock in the rubber tube is opened gradually until enough liquid has

passed from the graduated tube into the bottle A to reach the zero point of the tube b, after all the air bubbles have been expelled. The volume of liquid displaced by the brick is now in the graduated tube a, and can be noted at once. Further measurements are taken as follows: Without removing the brick enough liquid is removed through the faucet to bring the level of that in the graduated tube to the zero point, and after this has been drawn up in the tube by suction, a new piece of brick is put into the bottle. This procedure can be repeated until the bottle A can no longer contain new samples. Then the apparatus is emptied. Thus it is possible, without finding the specific gravity of the clay, to express the porosity of a clay object in percentages referred to the external dimensions. This expression is much clearer than the one which Dr. Avon, Olschewsky and I myself have heretofore made use of, that is, indicating the porosity by the

amount of water absorbed as compared with the specific gravity of the clay.

If V represents the external dimensions of the clay object whose porosity is to be determined, g the weight of the petroleum absorbed by it, s the specific gravity of the petroleum, the porosity may be expressed in this way:

$$P = \frac{\frac{g}{s} \times 100}{V}.$$

This expression of porosity contains also the elements necessary to determine the specific gravity of the clay. If G represents the actual weight of the clay object before saturation with water or petroleum, the specific gravity is represented by this formula:

$$S = \frac{G}{\frac{V(100 - P)}{100}}.$$

The following table shows the porosity of the clay objects resulting from several moldings. It is expressed in terms of the dimensions of the samples tested. The different mixtures mentioned in the table were kneaded when soft, then dried and pulverized again:

| MANNER OF MOLDING | 1. Yellow burning clay from Heegermühle 2. Red burning clay from Heegermühle 3. Two parts of No. 1 and one part of No. 2 4. One part of No. 1, One part terra cotta from clinker bricks 5. One part of No. 1, Two parts of terra Cotta 6. One part of No. 1, Two parts quartz Sand | | | | | |
|--|---|------|-------|-------|-------|-------|
| | Porosity expressed in percentages | | | | | |
| Pressed wet..... | 27.2 | 23.9 | 26.2 | 21.8 | 19.4 | 17.9 |
| Pressed wet and remolded when of the consistency of leather..... | 25.4 | 23.7 | 24.4 | 21.4 | 18.2 | 16.3 |
| Pressed dry..... | 32.1 | 24.9 | 25.4 | 23.2 | 23.1 | 22.6 |
| Pressed in a clammy condition, full pressure..... | | 19.9 | | | | |
| Clammy condition, half pressure... | | 30.2 | | | | |

This shows that it is a mistaken idea to suppose that clay products of greater density can be secured by the hydraulic pressure of dry clay than by other methods of molding. In the cases before us the products molded on the hydraulic press from perfectly dry clay have, with a single exception, in which the variation is not important, much greater porosity than those with which wet molding was employed. On the other hand, when clay of a clammy moistness was molded on the hydraulic press the density of the mud was essentially increased.

There is, however, a serious objection to the use in actual practice of clay so little moistened that it possesses as yet no plastic properties in the real sense of the word, and therefore undergoes a minimum of shrinkage in drying. Clay mud, which possesses a certain slight amount of moisture, can not easily be converted into a sufficiently fine powder, whereas clay fully dried can be reduced to this condition much more easily.

As might be expected from theoretical considerations, the density of clay which is re-pressed in a leathery condition is not essentially greater than that of the wet molded clay.

The advantage of re-pressing consists especially in the production or the reproduction of exact shapes when the clay has such a degree of moisture that it will no longer shrink appreciably in drying, and in the avoidance of cavities caused by imprisoned air bubbles, which are difficult to remove when wet molding is employed.

Of no less interest than the influence of molding upon the density of the raw clay is the behavior of the same samples in the fire.

A slice of a dry pressed flagstone secured from each of the mixtures shown in the above table was laid upon a terra cotta slab and six such slabs, each bearing a course, were distributed in the same set of cases in the red heat of the gas kiln in such a manner that each had a different temperature. This was accomplished by setting one course of samples directly beneath the roof of the kiln, another on the bottom, and the others at intervals of height of about 30 centimeters. The temperature of the kiln with a rebounding flame was, beneath the roof, the beginning of a white heat, that at the bottom somewhat above the melting point of silver. If we estimate the temperature at these two points as 1,250 to 1,000 deg. C and assume that the heat decreased gradually within these lim-

its from bottom to top, then for each course of samples there must have been an increase in temperature of 50 deg. C. from below upwards. In reality the difference in temperature was probably less, since the estimate of the difference between the top and bottom was probably too high.

The porosity of the samples after the burning is shown in the following table:

| Temperature in burning | No. 1 | | No. 2 | | No. 3 | No. 4 | No. 5 | No. 6 | Degree of burning of the clay from Heegermühle when molded wet | |
|-----------------------------------|------------|----------------------------|-------------|----------------|----------------|----------|----------|----------|--|--------------------------|
| | Molded wet | Pressed when perfectly dry | Pressed dry | Pressed moist | Pressed dry | | | | | |
| | | | | Full pressure* | Half pressure* | | | | | |
| | | | | | | | | | | |
| | | | | | | | | | | |
| Porosity expressed in percentages | | | | | | | | | | |
| A. 1000° C | 33.1 | 38.2 | 19.3 | 16.8 | 17.7 | 29.9 | 26.2 | 25.5 | 29.2 | Light to medium fire |
| B. 1050° C | 29. | 35.7 | 16.2 | 11.9 | 14.3 | 22.1 | 21.1 | 23.2 | 28.6 | Hard fire |
| C. 1100° C | 1. | 18.1 | 9.2 | 4.3 | 7. | 1.3 | 4.3 | 10.1 | 28.2 | Yellowish green clinkers |
| D. 1150° C | 0. | .2 | 2.4 | 2.2 | 2.5 | 1. | 2.1 | 1.8 | 23.6 | Edges rounded |
| E. 1200° C | volatile | volatile | 2.4 | 3. | 2.4 | volatile | volatile | volatile | 21.2 | } Widely spreading |
| F. 1250° C | volatile | volatile | 2.1 | 2.4 | 2.4 | volatile | volatile | volatile | 15.5 | |

If this table is compared with the preceding one, it will be seen that all the samples in which the calcareous clay of Heegermühle is present show a considerable increase in porosity at the lowest temperature applied. This is due to the loss of the chemically combined water and the carbonic acid. In the ferruginous clay, No. 2, the porosity was undoubtedly increased even at a lower temperature. But this is more than offset by the fusion which has begun.

The most striking thing in this table is the difference in be-

*The pressure exerted by the hydraulic press is about 200,000 kilograms, i. e., in making blocks 15 x 15 centimeters, 889 kg. to the square centimeter. When only the larger air pump is used the measurements of the hydraulic press show a pressure of 29,000 kg. or 129 kg. to the sq. cm., assuming that the pressure of the workmen at the pump handle is equal to 60 kg.

havior of the material in the course of condensation. In the case of the calcareous clay the condensation takes place very rapidly within a range of temperature of 50 deg. C. The manner of molding and the presence of admixtures which shrink little or not at all, may retard somewhat the rapid shrinkage, yet it is never so greatly retarded as in the case of non-calcareous material, where the range of temperature is over 100 deg.

The reason for the rapid shrinkage of the calcareous clay is to be sought in the fact that the lime mixed with it does not have any chemical action until a very high temperature is reached, but then becomes volatile very quickly, while in non-calcareous clay such an energetic action which affects the fusing point of the compounds cannot take place at all.

Moreover, the same phenomenon occurs in other kinds of clay mud.

An experienced manufacturer of porcelain, who has had occasion to use together different kinds of porcelain mud, told me he had found in actual practice that when the porcelain mud contained marble as a flux the condensation began at a higher temperature than when a great amount of feldspar was used; that, however, complete closure of the pores and transparency occurred at a lower temperature in the former case.

This difference in behavior is of importance in many branches of the clay industry, in which it is necessary to produce products of regular shape and of perfect density, which must therefore shrink rapidly under all circumstances, for it is clear that aside from the actual extent of shrinkage the time in which it is accomplished must have a great influence upon the preservation of the uniform shape.

Up to the present time it has not been possible to determine the inner relation of the density of clay mud to its chemical composition and structure, at least in the impure and coarser materials, since the conditions are greatly complicated by the presence of various constituents which cannot be isolated, and whose effect upon the porosity of the material has not been determined.

In order to secure some light upon this subject it seems best to start with pure varieties of clay mud, whose composition is definitely known, and in connection with these discuss the following questions: 1. What is the influence of the proportion between the alumina and the lean constituents? 2. What effect

upon the density is produced by the difference in the kind of alumina?

In order to find an answer to these questions, two series of clay muds were prepared, the corresponding samples of which possessed the same chemical composition, but in one case the bonding alumina was taken from a pure, but short kaolin, in the other, from a very plastic clay.

The composition of these two series of mud was as follows:

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---------|---------|---------|---------|---------|---------|---------|---------|
| Alumina ($\text{Al}_2\text{O}_3, 2\text{SiO}_2 + 2\text{H}_2\text{O}$) | % 25 | % 30 | % 35 | % 40 | % 45 | % 50 | % 55 | % 60 |
| Feldspar ($\text{K}_2\text{O Al}_2\text{O}_3, 6\text{SiO}_2$) | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 |
| Quartz (SiO_2) | 65 | 50 | 45 | 40 | 35 | 30 | 25 | 20 |

In series A the alumina was secured by mixing with kaolin from Pilsen, in series B by using the fat clay from Ebernhahn near Coblenz. The composition of these materials was as follows:

| | | |
|----------------|------------------------|-------------------------|
| | A. Kaolin from Pilsen. | B. Clay from Ebernhahn. |
| Alumina | 94.89 per cent. | 75.23 per cent. |
| Feldspar | 2.21 " " | " " |
| Quartz | 2.90 " " | 24.77 " " |

From these figures the amount of clay or kaolin, feldspar and quartz necessary for the admixture, can be computed.

The feldspar and quartz were used in the form of extremely fine powder, such as is employed for mud and glazes in the manufacture of porcelain. Although the corresponding samples in the two series had like chemical properties, their physical properties were quite different, corresponding with the differing properties of the alumina.

The muds of series A were short, even in the samples which contained the most alumina, and dried up into a mud which was easily rubbed to a powder and had marked de-coloring properties. The muds of series B were still quite plastic, even in the leanest samples, and dried up into a hard mud with little de-coloring power.

Those muds containing alumina in large quantities presented a smoothly polished surface when scratched with the finger nail, while even those containing the greatest amount of alumina in series A presented a dull, chalky surface.

From the 16 samples of mud in the series A and B, sample bricks were made which were tested for porosity in the manner described above, the conditions being as follows:

1. Dried in raw state at 120 deg. C.
2. Burned at the melting point of silver, about 960 deg. C.
3. Burned at the beginning of a luminous white heat, 1,200 to 1,300 deg. C.
4. Burned in heat used for porcelain, the melting point of forged iron, about 1,500 deg. C.

The burning was carried out gradually in each case with the same samples, two being used together, and all the samples were burned in the same terra cotta case.

The samples were molded when wet in a bronze mold, and when a leathery consistency was reached were repressed till the edges were perfectly sharp.

The result of the test for porosity and the corresponding shrinkage are given in the following tables:

A. Alumina from the kaolin of Pilsen

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|-----------------------------------|------|------|------|------|------|------|------|------|
| Porosity when raw | 33.6 | 36. | 36. | 37.6 | 37.8 | 38.2 | 38.6 | 38.8 |
| " " at 960 deg. | 33.8 | 36.2 | 36.2 | 37.7 | 37.4 | 38.2 | 38.5 | 39. |
| " " 1300 " | 1. | 1.8 | 1.9 | 2.6 | 1.7 | 1.7 | 1.5 | 2.6 |
| " " 1500 " | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Linear shrinkage at 950 deg. | 0 | 0 | 0.2 | 1.5 | 0.7 | 0.9 | 1.3 | 1.7 |
| " " " 950—1200 deg. | 10.7 | 11.7 | 11.7 | 11.7 | 11.5 | 11.6 | 11.3 | 11.2 |
| " " " 1300—1600 deg. | -2.3 | -1.2 | -1.3 | -1. | -0.9 | -0.2 | 0.2 | 0.3 |
| Total shrinkage | 8.4 | 10.5 | 10.4 | 10.7 | 10.6 | 11.4 | 11.5 | 11.5 |

B. Alumina from the clay of Ebernahn.

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|----------------------------|------|------|------|------|------|------|------|------|
| Porosity when raw | 26.6 | 26.9 | 27.4 | 28.3 | 28.2 | 28.3 | 29.7 | 29.8 |
| " " at 960 deg. | 28.2 | 27.2 | 27.6 | 28.1 | 26.2 | 25.9 | 26.2 | 25.1 |
| " " 1200—1300 deg. | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Shrinkage at 950 deg. | 2 | 6 | 5 | 1.2 | 1.7 | 1.9 | 2.3 | 2.6 |
| " " 1200—1300 deg. | 7.7 | 7.4 | 7.7 | 7.1 | 6.8 | 6.4 | 6.1 | 6. |
| Total shrinkage | 7.9 | 8. | 8.2 | 8.3 | 8.5 | 8.3 | 8.4 | 8.6 |

All the specimens were swollen and spotted in the porcelain roasting fire.

A comparison of the figures in the first horizontal row shows that there is uniformity only in this, that the density increases slightly in the unburned mud when lean substances are added.

In the second horizontal row the porosity of the muds con-

taining kaolin remains unchanged, in spite of the loss of chemically combined water, while in the samples of plastic clay a slight but noticeable condensation has taken place, especially in the less lean samples.

This is surprising, since both kaolin and plastic clay belong to the fireproof materials, and at the relatively low temperature to which they were exposed, i. e., the melting point of silver, we cannot suppose that any softening took place. This is even less probable from the fact that the most easily fused constituent of the different muds, feldspar, does not show the least indication of softening at this temperature. It must be, then, that condensation had taken place before this temperature was reached. In the samples A this was equivalent to the shrinkage produced by the escape of the chemically combined water; in the samples B it was somewhat greater.

Further evidence of this condensation is the slight yet certainly demonstrable linear shrinkage of the samples. This shrinkage increases as the proportion of alumina is increased, so that the latter must be the cause of it.

It seems from this that the theory which a number of scientists formerly held, Olschewsky especially, and which I myself supported, is not correct. That is, that the shrinkage of the clay begins when the latter begins to soften and absorb by capillary action the liquefiable constituents. This theory cannot hold, at least for the relatively low temperature at which the clay gives up its chemically combined water, although it may be true of the higher temperatures at which partial fusion does undoubtedly take place.

This first shrinkage has a parallel perhaps in the shrinkage which many objects undergo when chemical decomposition takes place, in which solid and fusible elements are left behind. Examples would be carbonate of lime and magnesia, hydrate of alumina and many others, which likewise undergo a shrinkage which is often very considerable by reason of the loss of carbonic acid and water, although the substances which remain, lime, magnesia and alumina, are absolutely non-fusible, so far as we know. The reason for this condensation must be that the molecules are set in motion simultaneously with the loss of carbonic acid and water, and are deposited then in more compact form. Yet it cannot be assumed that partial liquefaction in the ordinary sense of the word takes place.

The figures show also that such a contraction of the clay mud is more vigorous, or at least occurs at a lower tempera-

ture, in the presence of alumina with marked plastic properties, than when the alumina of the kaolin is less plastic. Therefore at the melting point of silver the mixtures containing the largest amount of plastic clay have become more dense, while the corresponding mixtures with kaolin clay retain a looser structure, as in the raw condition.

At the higher temperature to which the samples in the third horizontal row were exposed, the heat was sufficient to soften one of the constituents, the feldspar. At this point the density of the mud was perfect or nearly so, and the maximum degree of shrinkage was reached.

At a still higher temperature, in the red heat of the porcelain kiln, the specimens containing kaolin underwent a negative shrinkage, that is, an expansion which is particularly conspicuous in the extremely lean samples and which is due to the well-known tendency of the quartz to expand in the transition from the crystalline to the amorphous condition, produced by a high temperature.

This agrees with the experiments formerly made by H. Rose, in which it was found that the specific weight of the porcelain diminishes, as the temperature rises. The expansion just described is only another expression of the same fact, for a diminution of specific gravity by means of expansion is imaginable only when there is no possibility of expansion through increase of porous space, as when porcelain is burned to transparency. However, it is always a question of the composition of the mud in the burning of porcelain.

In the specimens B, for which the plastic clay of Ebernhahn furnished the alumina, the possible expansion could not be measured, since the bricks were swollen and misshapen in certain spots.

The measurements of total shrinkage correspond perfectly to the porosity of the samples in both raw and slightly burned condition.

Still more striking than the differences in porosity due to the varying proportions of alumina and the constituents which are lean, non-plastic and free from water, are those due to the differences in the physical properties of the aqueous silicate of alumina.

While the differences in porosity in tables A and B amount to only a small percentage, the physical character of the corresponding muds in the two series varies widely.

When the composition is the same the density of the speci-

mens made from plastic alumina is much greater in the raw condition than of those made from the kaolin alumina, and consequently the total shrinkage and the malformation due to it are considerably greater in the kaolin specimen.

We might formulate as follows the results of the preceding investigation which will be of value for practical operations:

1. The shrinkage in clay mud of a given composition depends upon the relation existing between the porous space remaining after drying or resulting from evaporation at a low temperature and the external dimensions.
2. The danger of malformation increases in proportion to the extent of shrinkage, or porosity.
3. When porosity and shrinkage are equal, the malformation increases in proportion to the rapidity of the closure of the pores, or the range of temperature within which it is accomplished.
4. The density of raw clay mud is influenced by the manner of molding. The greatest compactness is secured by the powerful pressure of moist clay; next to this stands the re-pressure of molded bricks when the clay has the consistency of leather, and last, the simple molding and drying of wet mud. The loosest structure is produced by the mechanical pressure of perfectly dry powdered clay even when hydraulic pressure is applied within the range pressure found practicable up to the present time.
5. The porosity and consequently the shrinkage of mud in the fire diminishes in proportion as the quantity of non-plastic constituents to the alumina is increased in the finest particles which cannot be removed by washing.
6. Other circumstances being equal, the porosity and consequent shrinkage in the fire is less when the bonding alumina has more of the character of the soapy, plastic clays, and greater when it possesses the shortness of the kaolin clay.
7. The shrinkage begins at a lower temperature when the mud contains alumina with marked plasticity than when the alumina contains kaolin.
8. Fusibility is not the only criterion for the temperature at which the shrinkage of the clay begins.

What Properties Render Clay Especially Suitable for the Manufacture of Clinkers and Paving Brick?

The question has often been raised as to what are the best materials and the best methods to be employed in the manu-

facture of clinkers and the densely-fused clay bricks which are used in laying floors or in paving streets, and various views have been advanced as to the advantages of one sort of material or another.

Although scientific investigation has not been made in this direction, the first essential is clearly that the clay must soften so gradually in the fire as not to lose its form; and in burning and drying change in the dimensions should take place within the closest possible limits.

But in order to meet these requirements various conditions must be met in the chemical, physical and molecular composition of the material.

Some manufacturers say that red clays are best adapted for clinkers; others maintain that the yellow-burning, calcareous materials are better, because they contain the greatest quantity of fluxes and are more easily fused at a low temperature.

It is a well-known fact that in the manufacture of clinkers a great variety of materials is used with widely-differing properties. But there are two particularly characteristic properties to which we are to direct our attention. The constituents of the clay should be combined in such a way that a part of them will flux at the lowest possible temperature and form, to a certain extent, the bond in the fire for the other non-fusible elements.

On the other hand, a part of the constituents should be as fireproof as possible and little subject to chemical action from the fluxed material, and should be sufficient in quantity to form a body which will hold the softened mud together and prevent its complete reduction to a pulpy paste.

As a rule, the residue of feldspar and augite which are often present in clay forms the most easily fusible element, and next comes the real clay, which is often so fusible that it serves as a flux, but is sometimes difficult of fusion and assists in preserving the shape. Finally we have quartz as a constituent of the clay which helps to preserve the skeleton.

The best proportion for the materials which serve as a flux and those which preserve the shape has not yet been determined for the manufacture of clinkers. Probably the proportion is similar to that required in the manufacture of porcelain, where the easily fusible constituents form about $\frac{1}{4}$ or $\frac{1}{3}$ of the entire material.

A second point of importance is that the bricks should

undergo as little shrinkage as possible, and we must determine upon what factors this shrinkage depends.

Two kinds of shrinkage are to be distinguished, one which takes place in drying, and another which occurs during the burning.

The difficulties of manufacture caused by shrinkage in drying can be overcome with comparative ease. The shrinkage can be reduced to a minimum by working the clay stiff, or by re-pressing the bricks to correct warping, or by relinquishing the advantages of plasticity and securing the desired shape by hydraulic pressure of the dry clay.

It is much more difficult to control the shrinkage which takes place in burning. The greater the porosity of the clay after drying, the greater its shrinkage in the fire, for the clinkering process consists merely in the complete closure of the pores which are formed in drying or in burning by the evaporation of certain constituents. The difficulties in preserving the shape are lessened when the clay has little porosity after drying and has become dense by means of molding.

The degree of porosity depends essentially upon the character of the single constituents of the clay. The results of previous investigations, published in the *Notizblatt* and other journals, show the influence exerted upon the density of the clay by fine and coarse sand, or finer and coarser particles of terra cotta.

Another factor which has been disregarded up to the present time, is the nature of the bonding material, the real alumina, which has perhaps a greater influence upon the density of the clay than the lean materials which are naturally or artificially mixed with the clay.

Two different varieties of clay bonds are to be distinguished, differing in their physical character—the alumina which occurs in the kaolins and that occurring in the fat plastic clays.

These two bonding materials may be looked upon as identical in their chemical composition. The differences between them are no greater than those between single specimens of the same class. Yet in their physical properties they are different.

The alumina in the kaolins dries to a very soft, powdery mud, while that of the same chemical composition in the real plastic clay dries to a horn-like mud.

The porous space left in the clay in drying corresponds also to this difference of behavior in drying. The clays which contain as a bond the kaolin alumina, or one that is similar in character, are decidedly looser in structure than those which contain the alumina which dries to a horny mud, even though the lean materials are exactly alike in quantity and character.

The linear shrinkage varies greatly, according as the bond is taken from a plastic clay or a kaolin, when the chemical composition is alike in other respects.

I have had an opportunity to observe that in different kinds of mud which contained equal quantities of quartz powder and feldspar, and differed only in the point that the alumina came in one case from plastic clay and in the other from kaolin clay, the porosity in an air-dried state amounted to 26 and 39 per cent of the volume.

From this it can be seen that in the manufacture of clinkers those kinds of clay should be sought which dry to a firm mass. The kaolin clays should be avoided, and those varieties employed which dry up to a horny condition.

In using quite plastic alumina it is also possible to increase the quantity of the lean constituents without diminishing the plasticity of the mud. However, the density is greatly increased when a large proportion of lean constituents is present.

But where shall the manufacturer who has access to only a single clay bed get suitable materials for making clinkers? Not every one will be able to get materials for this purpose. But if there are in a certain bed strata differing in appearance and properties, suitable experiments will show which materials are relatively the best for the manufacture of clinkers. It will be found that it is those which contain the least clay-bonding substance, but which remain plastic and contain lean constituents in a finely-pulverized condition, so that they cannot be distinguished externally from clay.

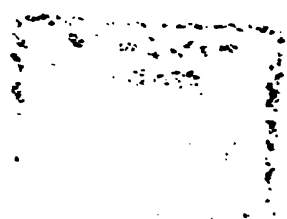
In other cases it may be practicable to secure other materials. Care must be taken to select so far as possible clays with plastic properties and not those which contain kaolin.

If calcareous clay is used in the manufacture of clinkers, the bricks may become quite dense in drying, but the structure will become loose again when the carbonic acid is expelled.

However, it is not impossible to make use of calcareous material, if the lean constituents are exceedingly fine and the clayey bond possesses sufficient plasticity so that it can be compressed into a very small amount.

I believe, therefore, that in many cases the fine, scaly brick material of North Germany can be employed in the manufacture of clinkers by mixing with it the plastic clays of the Lansitz.

Perhaps it will be possible in some places to procure the brown coal clays of the Lansitz and Saxony at prices which will make it profitable to mix these with the calcareous material. A second source of supply for North Germany is to be found in the north. In Sweden and on the island of Bornholm there are good beds of plastic clay. These deposits will probably be of importance for those brick plants which are situated on the Baltic Sea and can import the material easily.



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